This Page Is Inserted by IFW Operations and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problems Mailbox.

THIS PAGE BLANK (USPTO)



NTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:

B27K 3/34, 3/38

A2

(11) International Publication Number: WO 95/07807

(43) International Publication Date: 23 March 1995 (23.03.95)

(21) International Applicatin Number: PCT/NZ94/00095

(22) International Filing Date: 15 September 1994 (15.09.94)

(30) Priority Data:

HURILY Data.		
248685	16 September 1993 (16.09.93)	NZ
248686	16 September 1993 (16.09.93)	NZ
248687	16 September 1993 (16.09.93)	NZ
248688	16 September 1993 (16.09.93)	NZ
248689	16 September 1993 (16.09.93)	NZ
264172	4 August 1994 (04.08.94)	NZ
	•	

(71) Applicant (for all designated States except US): THE HOR-TICULTURE AND FOOD RESEARCH INSTITUTE OF NEW ZEALAND LIMITED [NZ/NZ]; State Highway 57, Palmerston North 5331 (NZ).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): HILL, Robert, Anthony [GB/NZ]; 54 Gordonton Road, Taupiri 2171 (NZ). RO-HITHA, Battagodage, Hemantha [NZ/NZ]; 31 Aurora Terrace, Hillcrest, Hamilton 2001 (NZ).
- (74) Agents: SIMS, Anthony, W. et al.; 29 Clarence Street, P.O. Box 759, Hamilton 2001 (NZ).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).

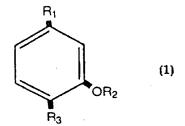
Published

Without international search report and to be republished upon receipt of that report.

(54) Title: METHODS AND COMPOSITIONS ADDRESSING SAPSTAIN, WOOD DEGRADATION, AND PESTS AFFECTING WOOD

(57) Abstract

The present invention is directed to compositions and methods for addressing problems of sapstain, wood decay, and/or pests in wood and wood-based materials. The invention relies on the use of a group of active compounds which are introduced into wood or wood-based materials. Various techniques for introducing different compositions are discussed. Different combinations of techniques and compositions can be used to provide short- to long-term protection to wood and wood-based materials, and in some instances may be used to treat materials already affected by sapstain, decay, and/or pest populations. The active compounds comprise one or more members of a group comprising: terpene derivatives such as derivable by the chemical or bio-technology processing of α - and β - pinene; β - unsaturated aldehydes and ketones; disubstituted mono-phenols, and mono-substituted diphenols of general formule (1), where: R_1 = alkyl, aryl, alkoxy; R_2 = H; R_3 = alkyl, aryl, alkoxy; or: R_1 = alkyl, alkenyl; R_2 = H; R_3 = OH; or: R_1 = alkyl, alkenyl; R_2 = CH3; R_3 = OH.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

	•				
AT	Austria	GB	United Kingdom	MR	Mauritania
ΑU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	Œ	Ireland	NZ	New Zealand .
BJ	Benin	rr .	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic	SD	Sudan
CG	Congo		of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazaktistan	SK	Slovekia
CM	Cameroon	Lī	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	ŪA.	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	Prance	MIN	Mongolia	VN	Viet Nam
GA	Gabon			414	TICE ITAME

5

15

20

25

30

35

METHODS AND COMPOSITIONS ADDRESSING SAPSTAIN, WOOD DEGRADATION, AND PESTS AFFECTING WOOD

TECHNICAL FIELD

The present invention is directed to problems commonly included under the general terms sapstain, and wood degradation, including degradation by both plant and animal life. The present invention discusses methods and compositions based on a group of active compounds, many of which are also naturally occurring, for addressing at least one of the problems of sapstain, wood degradation, and pest infestation or attack. Preventative and curative aspects are also considered.

10 BACKGROUND ART

Timber, wood, and cellulose fibre based products are used extensively throughout the world. In many instances they are used where a long life is expected, such as for building and construction materials. However many of these materials may be affected or degraded by a range of problems including sapstain, fungal degradation, and/or pest infestation or attack.

Sapstain is a discolouring disorder affecting many materials but most prevalently timber. Sapstain is a general term used in the industry and generally refers to the effects of any one or more of a range of organisms which produce discoloration. Over 1150 fungal species from 269 genera are known (with at least another 66 genera being known which comprise unidentified species) which can result in sapstain problems in timber. However, only a relative few of these are responsible for the majority of sapstain problems. In New Zealand, it is Ceratocystis picea which is responsible for the majority of sapstain problems. Other prevalent species include Ceratocystis sp.., Diplodea pinea, Leptographium sp., Graphium sp., Alternaria tenuis, Cladosporium herbarum, and Cytospora sp. The most predominant sapstain grouping is the Ceratocystis complex which includes the genera Ceratocystiopis, Ceratocystis, Ophiostoma and Sphaeronamella.. Other organisms of concern include Ceratocystis anamorph genera which include: Chalara, Graphium, Hyalorhinocladiella, Knoxdaviesia, Leprographium, Phialographium and Sporothix. Other important sapstain genera include: Alternia, Aurebasidium, Botryodiplodia, Cladosporium, Diplodia and Phialophora.

The problems arising from sapstain are primarily cosmetic and due to the unwelcome pigmentation resulting from the growth of a fungus, which in most cases establishes itself in and follows the parenchyma of woody material. As many timbers are valuable for their grain and appearance, sapstain can enormously devalue such timbers. Some international markets will not accept timber with any visible signs of sapstain, despite

sapstain not usually affecting the structural integrity of the time. However, it is noted that the presence of sapstain can lead to infection by other structurally damaging disorders by wood degraders such as white wood rot, <u>Peniophora gigantea</u> (the greatest problem in New Zealand), <u>Corticum sp.</u>, and <u>Schizophyllum commune</u>.

Wood degraders of concern include: Corticum sp., Ordontia bicolor, Peniophora gigantea (most important species), Polyporus volvatus, Poria vaillantii, Trametes cinnabarina (Coriolus sanguineus), Trametes serialis, Trechispora brinkmanni, Trechispora raduloides; and the soft rot fungi: Bisaporomyces sp., Cephalosporium sp., Chaetomium globosum, Coniothyrium sp., Helicomyces sp., Helicosporium aureum, Coriolus versicolor, Formes, Heterobasidion annosum, Lentinus lepideus, Lenzites, Peniophora, Phellinus weirii, Polyporus, Poria.

Healthy, growing trees will generally show a resistance to sapstain and it would be exceptionally rare for a living tree to be afflicted by the disorder. The main problems of sapstain occur once a tree has been felled and its wood exposed to the environment. Typical sapstain susceptible areas are exposed portions of a felled tree such as the cut base or any branches which have been removed. Trees which are sometimes left in the bush, or in a loading yard for several months are particularly susceptible to sapstain originating at these exposed portions. Often trees are debarked and may be exposed to the environment for up to several months before being transported or processed. In these cases the entire exposed face of the trunk is susceptible to sapstain.

A further major area in which sapstain may occur is in rough sawn timber which has not been chemically treated and may be stacked on an outside site in a timber yard for a considerable period of time. As an exceptionally high surface area of exposed wood is available for the establishment of sapstain organisms, and as the interface between adjacent planks often provide an ideal environment, rough sawn timber is the most vulnerable. It is further noted that most timber yards, as well as areas in which wood is stored, processed or transported through, have relatively high levels of spores of the various fungi responsible for many sapstains.

Wood degradation due to wood degrading fungi is another problem of the timber industry. While many organisms responsible for sapstain are not responsible for wood degradation, some are. Other organisms, such as many fungi, may predominantly affect the structural integrity of wood and are commonly referred to as wood degraders. These organisms raise more than cosmetic problems – the integrity of the timber itself is compromised and may infect other timber with which it comes in contact or proximity. Wood degraders of concern include

15

20

25

30

The prior art has attempted to address the problems of sapstain and wood degradation by the application of a chemically based fungicidal cocktail. This is generally applied to timber by immersion (only practicable for batches of rough sawn timber - the average tree trunk is too large for most dipping vats) or by spray application. These chemicals are generally based on phenolic compounds, synthetic compounds, or metal ions, none of which normally occur naturally within the timber being treated. The compounds are also, in most cases, highly toxic which does present some danger to the operators. However, a major problem afflicting the industry is that many of these compounds are also readily leached from the timber. This is also partially responsible for the fact that most treatments will only last three months, though under ideal conditions provide up to six months protection against most sapstain organisms. However, it will be appreciated that as most timbers are stored at specific locations, leaching of chemicals which do not occur naturally in the timber will be concentrated in the ground in these locations. Most timber yards and storage sites where wood treatment has occurred generally exhibit very high levels of these toxic materials and there is considerable concern over the subsequent transport of these chemicals into nearby streams and the environment.

Some fungal species are developing an increased resistance to the compounds currently used by the industry. Given the limited number of cost effective fungicidal agents used by the industry, a significant problem will arise if alternative methods or compositions are not made available.

Pest infestation is another concern of the industry. Some preservative agents effective against fungi are also effective at preventing pest and insect infestation. However, while a wide range of chemicals are used as pesticides, they do not usually exhibit antifungal properties. Most modern insecticides are synthetically manufactured and usually specific in their action. Quite often they have been used to the extent that many targeted pest species have developed a resistance. This has required the continual development of new pesticides to keep pace with any inbred immunity in targeted pest populations. This, in combination with high toxicity of many pesticides to other animal life, has lead to speculation that maybe nature has succeeded where science has not — many natural pesticides and pest repelling agents are still effective in their roles in nature and are often a plants main protection against certain types of infestation. This could perhaps be partially due to nature not relying upon these agents on such a wholesale scale as mankind, or perhaps nature has evolved a range of substances that many insects are less likely to adapt to.

35 There has been recent interest in the use of natural products as insect controlling agents and this may be partially motivated by the currently fashionable environmental

5

10

15

20

25

movement. Many countries also have strict controls on agricultural imports, refusing to accept goods which have been treated with certain pesticidal agents, or which exceed a certain residue level. However, most of this research appears based on crop and agricultural spraying and has not been generally directed to the timber and building industries. In this field, longer protection is generally desired than the short-term requirements of agricultural crops.

The toxic effect of pesticides on the environment and food chain is of as much, if not more, concern as the leaching of wood preservative chemicals. In many cases, synthetic insecticidal agents are alien to the environment and are not well accepted nor processed by the environmental food chain. The use of a combination of synthetic fungicidal and pesticidal agents for application to timber accentuates the problem. With a wave of increasing environmental concern, it is possible that nations may place restrictions on chemicals used on imported timber, in much the same manner as there are controls on pesticides used on certain items of agriculture imported into various countries.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

DISCLOSURE OF INVENTION

- According to one aspect of the present invention there is provided a method for addressing at least one of wood degradation, sapstain and pests, in wood or wood based materials comprising the incorporation or application to the wood or wood based material of a composition comprising at least one member of a group of active substances comprising:
- 25 terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.
- According to a further aspect of the present invention there is provided a method for conferring medium to long-term protection to wood and wood-based materials against at least one of pests and organisms responsible for either or both sapstain and wood degradation, said method comprising the impregnation into said timber or timber-based material of at least one member of a group of active substances comprising:

terpene derivatives such as derivable by the chemic for biotechnology processing of α - and β - pinene;

- β- unsaturated aldehydes and ketones;

5

10

20

3NSDOCID: <WO 9507807A2>

disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

Formula 1

Where:

 $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = aikyl, aryl, alkoxy$

OR:

 $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

Phenolic Compound

 R_1

 R_3

OR:

 $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

 $R_3 = OH$

According to a further aspect of the present invention there is provided a method of conferring short to medium term control of at least one pest, sapstain and/or wood degrading organism in freshly felled or milled timber comprising the surface application to at least freshly exposed faces of a composition comprising at least one member of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- β- unsaturated aldehydes and ketones;
- disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to a further aspect of the present invention there is provided a method for addressing at least one of wood degradation, sapstain and pests, in wood comprising the administration to the wood of at least one substance occurring naturally within timber of the genus, said substance(s) being members of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- β- unsaturated aldehydes and ketones;
- disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to a further aspect of the present invention there is provided a method of treating cutting and pruning wounds on trees and plants comprising the application of a composition comprising at least one member of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- β- unsaturated aldehydes and ketones;

5

20

25

30

disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to a further aspect of the present invention there is provided a composition for addressing at least one of wood degradation, sapstain and pests in wood and wood-based products comprising at least one member of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- 15 β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to another aspect of the present invention there is provided a composition, substantially as described above, in which a chosen active substance comprises at least one of α -terpineol, α -terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, and hydroxy-citronellal, furfural, ionone, pine oil, and tea tree (Melaleuca alternifolia) oil.

According to another aspect of the present invention there is provided a composition, substantially as described above, in which the chosen members are naturally occurring within, or a derivative of substances naturally occurring within, the timber being, or present within the material being, treated.

According to a further aspect of the present invention there is provided a composition having an adverse effect upon one or more organisms of a group comprising pests affecting wood and wood-based materials, and sapstain responsible and wood degrading organisms, said composition including at least one member of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- β- unsaturated aldehydes and ketones;
- disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to a further aspect of the present invention there is placed a composition for addressing either or both sapstain and wood degradation in timber, said composition including at least one member of a group of active substances comprising:

- terpene derivatives derivable by the chemical- or bio- technology processing of α and β pinene;
- β- unsaturated aldehydes and ketones;

5

20

30

disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to a further aspect of the present invention there is provided a composition for use in coating wounds and cuts in trees and plants, said composition capable of forming a protective barrier over the area to which it is applied, and including at least one member of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- 15 β unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

According to another aspect of the present invention there is provided a preservative composition for wood and wood-based materials comprising at least one member of a group of active substances comprising:

- terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
- β- unsaturated aldehydes and ketones;
- disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1.

For most embodiments of the present invention, use will be made of one or more substances which fall within a 'group of active substances' comprising three main categories. These categories, which will be discussed below, are:

- terpene derivatives such as those derivable by the chemical- or bio- technology processing of α and β pinene;
- disubstituted mono-phenols, and mono-substituted diphenols of the general formula shown in Formula 1, and
- β- unsaturated aldehydes and ketones.
- Typically the active substances are naturally occurring, though the active substances which are used need not be derived from natural sources but may be synthetically prepared.

The term 'pest control' where used herein shall generally refer to actions which influence pests within the affected area. Generally this will include repelling pests, as well as causing the death of the pest. It will also include affecting pests by rendering them to a passive state, and effects which minimise their population or reproduction. In the context of the present invention, pest control will generally be predominantly concerned with either directly or indirectly minimising pest damage to targeted areas.

The term 'pest' as used herein will generally refer to animals, rather than plants. Local pests such as insects manifesting themselves in timber and mill sites have been a subject of preliminary trials on woods samples. However it is envisaged that the results may be extrapolated to apply other pests of interest in agriculture, horticulture and many other fields. Typically the term pest will refer to arthropods affecting wood, timber and woodbased products. Generally such pests will comprise a member of one of the classes of insects, (including Hymenoptera and Coleoptera), and arachnids though the term pest will also include non-arthropods such as worms and molluscs affecting wood and timber etc.

It should also be noted that it is envisaged that not all selected active agents according to the present invention will be equally effective against all types of pests, just as many known pesticidal agents are not effective in all cases. Consequently, some minor trial and experimentation may be required by persons wishing to optimise the invention for specific applications. It is envisaged that this will be well within the abilities of a skilled addressee of the art in light of the description given herein.

The term 'wood' shall generally include woods, woody materials, timber, and logs etc. within its definition. 'Wood based materials' will generally comprise materials manufactured from 'wood' and shall generally include most 'cellulose fibre based materials' comprise materials manufactured from, or containing, 'wood' and/or other non-woody plant materials (usually including or based on the fibres). In many instances the materials will be those intended for use in the building, construction and related industries.

TERPENE COMPOUNDS

The first category comprises terpene derivatives which are generally those derivable by the chemical- or bio- technology processing of α- and β- pinene. In most cases these terpenes and their derivatives are naturally occurring though in many cases may be obtained by chemical- and bio-technology processes on α- or β-pinene including those shown in Formulae 2: α-terpineol (5), α-terpineol acetate (6), linalool (7), citral (geranial (8) + neral (9)), geraniol (10), citronellol (11), citronellal (12) and hydroxy-citronellal (13).

5

10

15

20

The compounds appear Formulae 2 are but a useful cross—on of the more well known terpene compounds derivable from α - or β -pinene, which may be used with the present invention. The various reactions comprising chemical, biochemical and biological transformations of α - or β -pinene to mono-terpene compounds are well documented and will not be repeated here. However, preliminary trials by the applicants have indicated that virtually all of these compounds will exhibit some sapstain controlling effects, albeit some greater than others. Consequently the reader should be aware that Formulae 2 is not an exhaustive list of all the preferred terpenoid compounds, and that the designated terpenoid group will include other monoterpenoids, including: terpinen-4-ol, pulegol, isopulegol, β -terpineol, γ -terpineol, δ -terpineol, nerol, geraniol, and citronellol.

It is noted that while some of the prior art have investigated the use of pine oil (which often contains a high proportion of terpenoids) for various applications, the main use of pine oil in the art is as a bactericidal agent effective against gram negative bacteria. The use of pine oil as a solvent and degreasing agent is also well known though there appears to have been no research into its use as a fungicidal agent, nor its use in addressing the problems associated with sapstain or pest infestation.

5

Members of the designated terpenoid group are generally less toxic than those of compounds currently used for addressing sapstain, wood degradation or pests. It is also likely that their use will be less objectionable to many authorities and possible problems associated with trade barriers to products using conventional toxic compounds may be minimised.

A range of compositions may be prepared for use in the application of the preferred terpenoid compounds (i.e. members of the designated terpenoid group). Pine oil, depending on its source and method of extraction, is typically high in terpineol and other terpene compounds. A composition according to the present invention may therefore comprise solely pine oil, or a dilution thereof. Tests have indicated that while pine oil may be diluted with other solvents or carriers, a composition with a concentration of 25% pine oil or greater is most preferred for many of the application methods. In the tests the pine oil was manufactured by Eka-Nobel NZ Limited at Mount Maunganui, New Zealand.

15 PHENOLIC COMPOUNDS

5

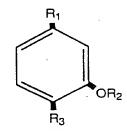
10

20

The second category comprises a group of phenolic compounds with typical compositions comprising at least one member of a designated phenolic group. In most cases these phenolics and their derivatives are naturally occurring though may be synthetically derived. Typically the preferred phenolic compounds comprise members of a designated phenolic group comprising:

Phenolics of the following general structure (Formula 3) either singly or as major components in mixtures of natural or synthetic origin.

Formula 3



Where:

 $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

e.g. thymol (1), carvracol (2) and related ortho, meta disubstituted phenols – refer Formulae 6

Phenolics of the following general structure (Formula 4) either singly or as major components in mixtures of natural or synthetic origin

Formula 4

5 Where:

$$R_1 = alkyl, alkenyl$$

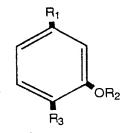
$$R_2 = H$$

$$R_3 = OH$$

e.g. 4-ethyl resorcinol (3) and related diphenols - refer Formulae 6

Phenolics of the following general structure (Formula 5) either singly or as major components in mixtures of natural or synthetic origin

Formula 5



Where:

$$R_1 = alkyl, alkenyl$$

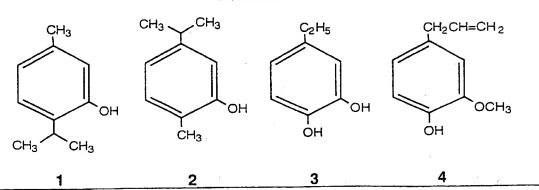
$$R_2 = CH_3$$

$$R_3 = OH$$

15

e.g. eugenol (4) - refer Formulae 6

Formulae 6



A range of compositions may be prepared for use in the application of a preferred phenolic compound (i.e. members of the designated phenolic group). Thyme oil, depending on its source and method of extraction, is typically high in thymol, a phenolic compound. A composition according to the present invention may therefore comprise solely thyme oil, or a dilution thereof. Tests have indicated that while thyme oil may be diluted with other solvents or carriers, a composition with a concentration of 25% thyme oil or greater is preferred for many of the application methods.

β-UNSATURATED ALDEHYDES AND KETONES

The third category comprises β -unsaturated aldehydes and ketones. In most cases the preferred aldehydes and ketones are naturally occurring, and may be derived from natural products though may also be synthetically derived. Non-naturally occurring β -unsaturated aldehydes and ketones may also be considered – it is the β -unsaturation which distinguishes active aldehydes and ketones from the lesser or non-active compounds. Some specific examples of preferred β -unsaturated aldehydes and ketones include geranial (8), neral (9) and furfural (14) - refer Formulae 7. The preferred group also includes other predominantly naturally occurring β -unsaturated aldehydes and ketones including: pulegone, isopulegone, carrone, piperitenone, verbenone, ionone, myrtenal, perillaldehyde, and piperitone.

A range of compositions may be prepared for use in the application of the preferred β -unsaturated aldehyde and ketone compounds (i.e. members of the designated aldehyde and ketone group). Preliminary trials have indicated that a composition with a concentration of 25% active substance or greater is preferred for many of the application methods.

10

15

20

5

10

15

20

25

30

35

It is noted that while some of the prior art has investigated the use of terpenes, phenolics, aldehydes and ketones, they have predominantly been synthetic compounds which are not naturally occurring and with no direct relationship to naturally occurring compounds. There appears to have been little, if any, research into the use of the naturally occurring compounds (or their close analogues) as fungicidal agents, nor their use in addressing the problems associated with the specific problem of sapstain and/or wood degradation.

Research and trials by the applicants have shown that certain naturally occurring compounds, including those of the group of active substances, are very effective at addressing problems of sapstain, and often also wood degradation. Typically they are also effective at repelling or controlling pest populations. In many instances application of a member of the group can be used in a preventative manner to prevent the establishment of sapstain, and/or wood degrading organisms including pests. The preventative effects may be short to long term depending upon the compounds, methods and other substances incorporated.

In another role the compounds may be used to treat materials already contaminated with either or both sapstain or wood degrading fungus and halt its further spread or growth. The use of the compounds on pest infested wood may also be performed. The use of conventional insecticides to assist in the immediate control and eradication of existing populations may be performed. Further, some preliminary trials have indicated that in some cases the use of some compositions of the invention may reverse some of the visible effects attributable to some sapstain organisms.

As can be appreciated, there is an exceptionally large number of combinations of different timbers and materials, sapstains and wood degrading organisms, pests, as well as different members of the group of active substances. Consequently, some minor preliminary experimentation may be required to determine the effectiveness of each possible combination. Trials undertaken by the applicant have exhibited a general effectiveness of the named active compounds for commonly used timbers against the most prevalent sapstain organisms as well as wood-degraders and pests. In some cases the activity has been specific to various organisms though most have exhibited activity against a broad range of targeted organisms.

There are a number of potentially realisable advantages associated with use of the naturally occurring active compounds and their derivatives. Active compounds which are used may be naturally present in the wood or wood product to which they are applied. This is the preference as possible staining or incompatibility problems are minimised.

WO 95/07807 PCT/NZ94/00095 ·

Many copper based preservatives visibly stain wood and cannot always be used. Naturally occurring compounds in the wood are also less likely to adversely affect any structural characteristics of the wood.

This may be important both from a construction viewpoint and whether the treated wood still behaves like the natural wood - e.g. will it accept standard paints and finishes?

In some instances it may not be possible, or desirable to rely on an active compound found naturally in a wood - an example is where a second different compound is used to protect the wood against a broader range of fungi and/or pests. While active compounds are not naturally occurring in the wood in question are relied upon, compatibility problems could be minimised if the compounds occur in related timbers, or if the active compounds are similar or related to naturally occurring compounds in the wood or its related timbers.

Members of the group of active substances are generally less toxic to humans or the environment than those of currently used compounds for addressing sapstain, wood degradation and/or pest control. It is also likely that their use will be less objectionable to many authorities and possible problems associated with trade barriers to products using conventional toxic compounds may be minimised.

COMPOSITIONS

5

10

15

20

25

30

35

Typically any composition, according to the present invention for addressing at least one of sapstain, wood-degradation, and pests in the short to medium term will comprise at least 0.01%, and more preferably 0.5%, by weight (in total) or greater of one or more members of the group of active substances. However it should also be appreciated that higher concentrations (by weight) will generally provide a longer lasting effect. Wet or hard timbers may resist any impregnation of the active compounds so that higher concentrations may be sometimes desirable to ensure adequate wetting of, and impregnation into, exposed surfaces.

A wide range of methods may be employed for the short to long term preservation of wood, as well as cellulose fibre and wood based materials. Commonly a composition comprising at least one chosen active substance will form a base for many of the methods of use possible for the present invention. A composition may, for instance, comprise up to 100% of a substantially pure compound. However it is envisaged that many of these compounds will be extracted from natural sources and thus the composition may be an extract such as pine oil which is rich in terpenes (such as the various terpineols). Consequently, impure extracts and solutions of chosen active substances will often be used in the preparation of compositions.

Typically a preservative dium to long term) composition will prise at least 5% by weight in total of chosen active substances and more preferably 25% or greater. This is generally higher than for short term protection, which is mainly directed against, organisms responsible for sapstain (wood degradation is often a much longer term process; pest control is both a short and long term process). However the proportion of chosen active substances in a composition will depend upon a number of factors. One factor is a method of administration of the composition. For instance, application by the immersion of a targeted article may be amenable to lower concentrations (even less than 5%) of a chosen active substance as a greater volume of composition is generally absorbed by the article. Pressure and/or vacuum systems and other forced impregnation techniques may also suffice with lower concentrations of active components, or solvents.

In most compositions which are to be applied by spray application, concentrations (of active components) of 25% or greater (by weight and in total) are generally preferred. In compositions which are intended to be applied as a fumigant, higher concentrations of the preferred active compounds, as well as the absence or reduction of any solvents or carrier which are likely to depress the volatility of the group members, may be preferred. Volatile carriers and azeotropes which aid distribution of the active compounds and may be included.

Many compositions will include a suitable carrier or diluent. In some cases the carriers/diluents may be non-aqueous (though may be miscible with water) organic solvents in which the chosen active substances are fully miscible, or at least miscible at the concentrations being used. By way of example, the use of crude and hydrated turpentines may be considered. These may already include proportions of active components (according to their method of manufacture), though often the levels may need to be enhanced or other active components included to address possible resistance to individual substances. Other solvents, such as used in the paint industry, may also be considered. The flammability of many organic solvents may preclude or restrict their use in certain compositions or methods of application. On the other hand organic solvents may sometimes be preferable over water as the main diluent or carrier as it may not be desirable for timber to be subsequently kiln dried to remove excess moisture.

It has also been found that water may be used as a suitable carrier or diluent for many compositions. Initial trials used an emulsion of a terpene compound with water though a small amount of wetting agent was included. Again the presence of water in the spray emulsion did not appear to substantially inhibit the absorption of a sufficient amount of a terpene compound to inhibit subsequent fungal growth or its establishment. That water may be used as a diluent/carrier may also be of advantage as it is generally plentifully available in remote logging sites and does not require the use of flammable or expensive

5

10

15

20

25

30

solvents. The use of water may also inhibit any flammabhre, exhibited by any of active compounds or included solvents, which may be of advantage during periods of high fire risk.

In some aqueous compositions the chosen active substance(s) may be in a separate phase, or emulsion with the water. In other instances, a solvent miscible both with water and the chosen active substances may be used to produce a substantially homogenous phase. This may be advantageous if it accelerates the impregnation of an article with composition. However this will partially depend on the nature of the article. Where the article is wet (e.g. wet timber), compositions which allow some miscibility between chosen active substance and water may be useful if it accelerates transport of the chosen active substances into the timber or material.

Other agents and additives may also be incorporated into the composition. Commonly envisaged additives are wetting agents to promote the impregnation of a composition. Other possible additives include fungicidal, insecticidal or other common additives and treatments, to augment the preservative treatment. Compatibility of the chosen active substances with any additives should also be considered before use.

As can be appreciated, a wide range of concentrations and compositions are available and the exact formulation of a composition will depend upon the manner in which the composition is to be applied, as well as the nature of the article to which it is to be applied (porous/non-porous, wet/dry, end grain or not, etc.).

APPLICATION TECHNIQUES

It should be appreciated that while the major use of the present invention is seen to be in conjunction with wood and timber, many other wood, and cellulose fibre, based materials also may suffer from sapstain, wood degradation and/or pest infestation or attack. It is therefore also envisaged that the present invention may be employed to address the prevention, control and/or elimination of sapstain, degrading organisms and/or pests in a wide variety of materials. Consequently various application techniques may be relied upon.

Compositions of the present invention may be applied in a variety of manners. In most cases it is envisaged that a composition will be applied by spray to the material being protected or treated. In newly felled trees, it is envisaged that an operator equipped with a spray applicator and backpack reservoir will spray exposed timber as soon as possible after tree felling. If a significant period elapses, then repeat application may be required. This may be after several weeks or months, depending upon the conditions, composition and nature of application.

5

10

15

20

25

30

Newly exposed surfaces of timber should also be treated and debarking or milling operations. This will generally provide protection against sapstain fungi such as Ceratocystis and Diplodea, (see BACKGROUND ART for complete list) though will often also repel most insects. Short term wood degradation is generally not a problem though this problem will usually also be addressed.

If branches are trimmed then the exposed sites on the trunk should also be coated. While in many cases the spray sites on the trunk may be wet, it has been found that most compositions will readily allow the selected active compounds to impregnate into the exposed timber. Presumably this is because many of these compounds, and their related compounds, are already present in the timber and thus there is a natural affinity between the active compounds and the woody material. However this is but one explanation — it has been found in preliminary trials that a wet timber will not normally exclude, although it may slow, impregnation of a typically useful amount of one of at least the preferred terpene compounds into the timber. As many forests have a relatively high annual rainfall, and as most newly felled timber is wet, the general relative ease of impregnation may be a significant advantage.

An observed effect during the preliminary trials was an apparent synergism between emulsifiers and the active ingredients. The effectiveness of the active component appeared enhanced and the inclusion of surfactants or emulsifying agents in compositions may provide realisable advantages for some applications of the invention. The presence of pine oil, which exhibits some emulsifying capability, in some samples suggested improved results. It is possible that an emulsifier or surfactant increases penetration of the active component into the material, though this is not yet clear.

Longer term or greater protection may generally be achieved by relatively deep impregnation of chosen active substances. Solvents and carriers which are highly mobile within the timber or article could make spray application a viable option for greater penetration though saturation and/or high pressure spraying may also be an option. It is envisaged that in such cases the solvents/carriers will likely be organic, and perhaps volatile, in nature and may be derived or resemble natural products from the wood of the article – for instance turpentine which may also be a mineral turpentine.

A variation of spraying is fumigation where the components are substantially gaseous or vaporised techniques. However this technique is more likely to be used under controlled conditions of a timber yard or chamber than the open areas of a pine forest. Normal methods of fumigation may be used, including methods of increasing the volatility of the preferred terpenoid compounds (e.g. heating, forming azeotropes etc.).

5

10

15

20

25

30

5

10

15

20

25

30

35



Fumigation techniques may rely on heated air or elevated temperatures to help distribute a mist or vapour of chosen active substances. Such techniques may be ideally combined with heat and forced drying techniques though compatibility with the equipment being used would have to be considered. Potentially explosive fuel/air mixtures is one factor to be considered, and care should be taken to avoid such conditions, or suitable precautionary steps taken.

In order for fumigation techniques to be effective, it is envisaged that an atmosphere saturated or highly impregnated with chosen active substances would need to be created to reduce processing time. As a general rule it is expected that fumigation techniques will be less effective and require greater time than immersion techniques though this may not always be true, depending on the material. Fumigation techniques may be desirable where extensive wetting of an article with solvents and carriers is to be avoided. It may also be useful where an impregnation gradient other than that obtainable by immersion techniques is required. Further, fumigation type techniques may make more efficient use of composition components. The choice is largely up to the end user.

It is envisaged that fumigation may have advantages over some of the other techniques when it is practicable. For instance, fumigation may allow better access to areas relatively inaccessible to spray techniques - one example would be a stack of sawn timber. It may also be less wasteful of active compounds than immersion techniques which may rely on the use of carriers and diluents to reduce the amount of active compound used or absorbed, to an economical level.

Immersion techniques may often be used, and the likely solvent would be water (in general preference to more expensive or flammable solvents) due to the high volumes used. However, such immersion techniques may have a tendency to excessively wet the wood; the general preference for timber used in the building industry is for it to be dry. Extensive wetting may require kiln drying or other drying steps before the timber may be used. Organic solvents may avoid this problem, and if recycled could yield an economical process. A pressure/vacuum technique (this may be used in a fumigation (vaporised components) or immersion (liquid components) process) could be used, with a vacuum step removing excess solvents from the wood materials for reuse.

Immersion techniques may also take place under elevated temperatures and pressures to accelerate impregnation, and to increase its depth. It is envisaged that, in light of the description given herein, it would be well within the skill of an addressee of the art to construct or use existing apparatus to put these techniques into practice. There is no fixed limit to the pressures and temperatures which may be employed – the main consideration is that the article is not materially damaged or compromised by the process.

In some instances, and where practicable, chosen active substances and compositions may be included in manufacturing processes. For instance, it would be relatively simple to include these substances in a pulping or shredding process for wood. This could be useful for reconstituted timber products such as particle and ply boards.

Another method of use for the present invention is the application of compositions to materials already infected by sapstain and/or wood degrading organisms. In this role the primary purpose of the composition is to halt further spread of the organism. It will typically also act as a fungicidal agent killing any of the sapstain organisms present in the material. In some cases and where acceptable, a conventional fungicide may be included.

Where wood degrading organisms are also present, substances addressing these organisms may be included. For large scale use, immersion, spray and other described techniques may be relied upon. For more localised use, compositions may be painted, sprayed or rubbed on.

Some compositions may also be used to reverse the effects of sapstain organisms, and in some cases visible improvements in reduced staining may be achieved. However, this may not be achievable in every instance and will depend upon many factors including the degree of staining and the material being treated.

It is envisaged that many other methods of application of chosen active substances and compositions may be employed. In addition to the above techniques given by way of example only, various known and used techniques of the art may also be employed.

VARIATIONS & MODIFICATIONS

Modifications to the above methods may be implemented. One modification is to apply a second loss-reducing agent which may reduce leaching or release of the chosen active substance(s). This may be a substance of low volatility, or which repels the chosen active substances. It may also repel moisture. It may also provide a barrier layer.

Many waxy or oily substances compatible with timber and other materials are known and may be used. In some cases a shellac, varnish, paint or petroleum product (typically soluble emulsifiable but resistant to leaching) may suffice. By way of example only, shellacs could be incorporated into compositions having suitable solvents. Many epoxy materials are suitable for organic and aqueous based compositions. These may be used to bind or seal components into the timber. Consequently some compositions may resemble a paint or protective finish for wood and other materials and may sometimes be used as a decorative or finish coat.

In these examples it is envisaged that the depth of penetration of these larger compounds will be substantially less than the generally more mobile chosen active substances.

15

20

25

30

Consequently the inclusion of these loss-reducing agents in a composition may be sufficient, rather than having a second application step.

In some instances, conventional preservative and pesticidal agents may be used in cases where an article or material is already exhibiting signs of decay or attack. The additives may address the immediate problems while the chosen active substances provide a longer preservative effect.

BRIEF DESCRIPTION OF DRAWINGS

	BRIEF DES	CRIPTION OF DRAWINGS
	Figure 1	is a graph of the "RELATIVE GROWTH RATE OF SAPSTAIN FUNGI ON WOOD BLOCKS UNDER CONTROLLED CONDITIONS", and
10	Figure 2	is a graph of the "RELATIVE GROWTH OF SAPSTAIN FUNGI ON WOOD BLOCKS UNDER CONTROLLED CONDITIONS AT 48 DAYS", and
	Figure 3	is a graph of the "RELATIVE GROWTH OF SAPSTAIN FUNGI ON WOOD BLOCKS UNDER CONTROLLED CONDITIONS AT 90 DAYS", and
15	Figure 4	is a graph of the "RELATIVE GROWTH OF SAPSTAIN FUNGI ON WOOD BLOCKS UNDER CONTROLLED CONDITIONS AT 137 DAYS", and
	Figure 5	is a graph of the "EFFECTS OF VARIOUS TREATMENTS ON SAPSTAIN FUNGAL GROWTH WITH ACTIVE COMPOSITION ON INFECTED AGAR", and
20	Figure 6	is a graph of the "EFFECTS OF VARIOUS TREATMENTS ON SAPSTAIN FUNGAL GROWTH WITH ACTIVE CHEMICAL ON ROOF OVER LYING AGAR", and
	Figure 7	is a graph of the "MEAN VIGOUR OF FOUR FUNGAL COLONIES WITH VARIOUS CHEMICALS WHEN IN CONTACT AND WHEN AFFECTED BY FUMIGATION ACTION", and
25	Figure 8	is a graph of "the relative development of four sapstain fungi with different concentrations of $\;\;$ α -terpineol and pine oil when in contact with said fungi", and
	Figure 9	is a graph of "THE RELATIVE DEVELOPMENT OF FOUR SAPSTAIN FUNGI WITH DIFFERENT CONCENTRATION OF α -TERPINEOL AND PINE OIL WHEN SAID FUNGI ARE AFFECTED BY FUMIGATION ACTION FROM
30		CHEMICAL ON ROOF OF PETRI DISH".
	Figure 10	is a graph of "RESULTS OF BIOLOGICAL CONTROL OF SAPSTAIN AT MILL SITE A, TRIAL 1 OVER 6 MONTH PERIOD".



	Figure 11	is a graph of "RESULTS OF BIOLOGICAL CONTROL OF SAPSTAIN AT MILL SITE A, TRIAL 2 OVER 5 MONTH PERIOD".
	Figure 12	is a graph of "RESULTS OF BIOLOGICAL CONTROL OF SAPSTAIN AT MILL SITE B, TRIAL 1 OVER 6 MONTH PERIOD".
5	Figure 13	is a graph of "RESULTS OF BIOLOGICAL CONTROL OF SAPSTAIN AT MILL SITE B, TRIAL 2 OVER 5 MONTH PERIOD".
•	Figure 14	is a table of "SAPSTAIN GROWTH ON VARIOUS TIMBERS TREATED WITH VARYING CONCENTRATIONS OF PINE OIL".
10	Figure 15	is a graph of "RESULTS OF BIOLOGICAL CONTROL OF SAPSTAIN AT MILL SITE A, OVER A 5 MONTH PERIOD".
	Figure 16	is a graph of "RESULTS OF BIOLOGICAL CONTROL OF SAPSTAIN AT MILL SITE B, OVER A 5 MONTH PERIOD".
	Figure 17	is a graph of "INVERTEBRATES POPULATIONS OBSERVED ON EXPERIMENTAL PLOTS TREATED WITH VARYING COMPOSITIONS".
15	Figure 18	is a graph of "THE NUMBER OF INVERTEBRATE SPECIES OBSERVED ON EXPERIMENTAL PLOTS TREATED WITH DIFFERENT COMPOSITIONS"
	Figure 19	is a graph of "INSECT NUMBERS IN TREATMENTS AT MILLSITE"
	Figure 20	is a graph of "NUMBER OF INSECTICIDES AT MILLSITE TRIALS"
	Figure 21	is a graph of "SAPSTAIN INHIBITION BY PINE OILS ON WOOD BLOCKS"
20	Figure 22	is a graph of "SAPSTAIN INHIBITION BY PINE OILS ON WOOD CHIPS"
	Figure 23	is a graph of "SAPSTAIN INHIBITION AT MILL SITE 1, TRIAL 1"
	Figure 24	is a graph of "SAPSTAIN INHIBITION AT MILL SITE 1, TRIAL 1 (SPACED BLOCKS"
	Figure 25	is a graph of "SAPSTAIN INHIBITION AT MILL SITE 2, TRIAL 2"
25	Figure 26	is a graph of "SAPSTAIN INHIBITION AT MILL SITE 1, TRIAL 2"
	Figure 27	is a graph of "SAPSTAIN INHIBITION AT MILL SITE 3, TRIAL 1"



Example One

Long-term protection offered by pine oil in wood tablets in the laboratory

METHODS

Wood tablets (90mm x 50mm x 18mm) were cut from freshly sawn timber. The tablets were painted with a painter's brush with 2.5 ml/block of the following emulsion:

Table 1

Treatment	Pine oil concentration in emulsion
1	100
2	25
3	6.25
4	1.56
5	Control

The pine oil had a high percentage of α-terpineol, and was sourced from Eka-Nobel NZ Limited at Mount Maunganui, New Zealand.

The emulsions included 0.05% CITOWETTM, a proprietary wetting agent. A spore emulsion of FK48 fungus (<u>Alternaria sp.</u>) was then sprayed onto the tablets (4.5 ml/tablet) with a hand sprayer. 4 ml of water was added onto filter paper pieces placed on DETMOLDTM packaging SV1000 plastic containers. Wood tablets were placed on bent plastic straws and maintained at 20°C. After 48, 90 and 137 days the sapstain on wood blocks was assessed by 2 independent observers. Relative sapstain levels on all sides of the wood blocks were assessed.

RESULTS

10

15

20

25

Results indicate that the 100% pine oil (with 85% terpene alcohols) treatment differed significantly from the control and was still highly effective after 137 days. Pine oil concentrations of less than 25% were not observed to be significantly different from the control inside the containers.

Results indicate that the top and bottom surfaces of the wood tablets were the most susceptible (had the highest score), end grain having the next highest score which was significantly different from the top or bottom. Figure 1 shows the relative combined scores of sapstain of the five treatments.



Sapstain development on sides of the wood blocks was assessed and is summarised in Figures 2 - 4. It appears that the 25% pine oil treatment was effective for at least up to 48 days and that end grains (N, S) were generally more susceptible than the other sides. Pine oil 100% was effective up to at least 137 days on all sides of the blocks.

5 Continued observations show excellent control even after 51/2 months for the 100% pine oil treatments.

Example Two

Activity of pine oil fractions and their fumigant effects

The activity of four component fractions (Figure 5) of pine oil against sapstain fungi and their fumigant activity against four sapstain fungi was examined using potato dextrose agar plates.

Table 2
Pine oil fractions and treatments

Treatments/Fraction	Chemical of Agar	Chemical on roof
(predominant chemical)	-	•
1. PC500 (α-pinene)	√	
2. as above		\checkmark
3. PC600 (\(\beta\)-pinene)		
4. as above		\checkmark
5. PC560 (dipentene*)	$\sqrt{}$	
6. as above		√
7. PC593 (α-terpineol)	\checkmark	
8. as above		√
9. PC530 (pine oil [†])	\checkmark	
10. as above		\checkmark
11. Sterile water	\checkmark	
12. as above		\checkmark
13. Copper oxyquinolate	\checkmark	,
14. as above		√

^{*} major components: limonene and terpinolene

METHODS

Fungal spore suspensions from FK48 (<u>Alternaria sp.</u>) and FK63 (<u>Ceratocystis sp.</u>) were made with 0.025% Triton-X40. Mycelial homogenates of FK36 (<u>Ceratocystis sp.</u>) and FK64 (<u>Ceratocystis sp.</u>) were prepared under sterile conditions with a high speed

^{† 85%} terpene alcohols

blending attachment. Smears were made on PDA (potato dextrose agar) plates with $200\,\mu l$ of the prepared spore suspensions. Sterile filter paper discs (18mm) were impregnated with $30\,\mu l$ of the chemical fractions (Table 1). With each fraction, inhibitory effects when the chemical is placed on agar and when the chemical is placed on the roof of the lid was examined. Impregnated discs were attached onto the roof of the lid with melted PDA. The treatments used were as indicated in Table 2.

The pine oil fractions were supplied by Eka-Nobel NZ Limited in Mount Maunganui. The activity of these fractions was compared with the pine oil (85% terpene alcohols) also supplied by the same company.

10 RESULTS

5

15

Table 3 details the relative inhibition obtained with each chemical working with the four fungal types, FK36, FK48, FK63, FK64. Figures 5 and 6 show the comparative vigour based on the colour of the substrate of the fungal colony observed with pine oil fractions with all four fungi. Results indicated that with all four fungi samples, 85% pine oil was highly effective. There was a definite association of activity with α -terpineol. Both these materials had contact as well as fumigatory activity.

Table 3

Relative inhibition of four fungal strains observed with pine oil fractions when applied onto agar and onto roof of petri dish.

	Chemical on agar Inhibition of fungal development	Chemical on agar Growth on the discs	Chemical on roof Inhibition of fungal development
Fungus: FK36			
(Ceratocystis sp.)		-	
Chemical			
α-pinene	NI	Y	.NI
ß-pinene	NI	Y	NI
dipentene	VSI	N	NI
α-terpineol	I	N ·	I
pine oil *	I	N	Ι
sterile water	NI	Y	NI
copper oxyquinolate	I (r)	N	NI
Fungus: FK48	×		
(Alternaria sp.)			
Chemical			
α-pinene	NI	Y	NI
ß-pinene	VSI	N	NI
dipentene	NI	N	NI
α-terpineol	I	N	I
pine oil *	I	N	\mathbf{I}
sterile water	NI	Y	NI
copper oxyquinolate	I(r)	N	NI

Table 3 continued

	Chemical on		Chemical on
Table 3	agar		roof
continued	Inhibition of fungal	Growth on the discs	Inhibition of fungal development
	development		development
Fungus: FK63			
(Ceratocystis sp.)			
Chemical			
α-pinene	NI	Y	NI
ß-pinene	NI	Y	NI
dipentene	NI	Y	NI
α-terpineol	I	N	I
pine oil *	I	N	I
sterile water	NI	Y	NI
copper oxyquinolate	I(r)	N	NI
Fungus: FK64	·		
(Ceratocystis sp.)			
Chemical			
α-pinene	NI	Y	NI
ß-pinene	NI	Y	NI
dipentene	NI	Y	NI
α-terpineol	I	N	I
pine oil *	I	N ·	I ·
sterile water	NI	Y	NI
copper oxyquinolate	I(r)	N	NI

Key

5

I = inhibition observed

I(r) = inhibition in a definite ring form

NI = no inhibition

VSI = very slight inhibition

Y = yes

N = no

* = 85% terpene alcohols

The fraction containing α -pinene, β -pinene were not, however very active. Very slight inhibition (not measurable) on contact was seen with FK36 (<u>Ceratocystis sp.</u>) with dipentene. Occasionally dipentene stopped the fungal growth over the filter paper discs.

CONCLUSIONS

The main active components of 80% pine oil against all four sapstain fungi tested were terpineols. These compounds are seen to have contact as well as fumigatory activity against all fungi tested.

5 Example Three

Effect of pine oil and α -terpineol on sapstain fungi In this trial, the relative efficacy of different concentrations of pine oil and α -terpineol was examined.

METHODS

Fungal suspensions of FK48 (<u>Alternaria sp.</u>) and FK63 (<u>Ceratocystis sp.</u>) fungi and fungal blends of FK36 (<u>Ceratocystis sp.</u>) and FK64 (<u>Ceratocystis sp.</u>) were prepared. Smears were prepared with 200 µl of the solutions spread on PDA. Sterile filter paper moistened with 30µl of the following treatments were placed on agar as well as on the petri dish roof. Filter paper discs were glued onto the roof with melted PDA. The plates were incubated at room temperature and assessed in 7 days - refer Table 4.

RESULTS

20

Table 5 indicates the efficacy of various concentrations of pine oil and α - terpineol. Relative development of fungal colony was assessed on a scale of 0-10 and is presented in Figures 8 and 9. Both α -terpineol and pine oil had contact as well as the fumigant activity. In general both materials were active in the same degree. (Occasionally there were indications for α -terpineol to be slightly more active than pine oil). Activity was seen in concentrations 75% and 100%. In some cases with α -terpineol (FK64) there was inhibition at 50% but 25% was not effective on the agar plates.

Example Four

Two compositions, particularly suitable for application methods such as immersion, are detailed as follows:

Example 4A

Composition comprising, percentages by weight to a total of 100%.

5-100%

at least one member of the designated terpenoid group

30 0%-trace

wetting agents

0-50%

solvents miscible with water and said member(s) of designated

terpenoid group

0-95%

water

Table 4

Treatments	Concentration	Chemical on	Chemical on
		agar	roof
1. Sterile water		x	
2. Sterile water			x
3. Pine oil	25%	x	
4. Pine oil	25%		x
5. Pine oil	50%	x	
6. Pine oil	50%		x
7. Pine oil	75%	x	
8. Pine oil	75%		x
9. Pine oil	100%	x	
10. Pine oil	100%		x
11. α-terpineol	25%	x	
12. α-terpineol	25%		x
13. α-terpineol	50%	x	
14. α-terpineol	50%		x
15. α-terpineol	75%	x	
16. α-terpineol	75%		x
17. α-terpineol	100%	x	
18. α-terpineol	100%		x
19. copper oxyquinolate		x	
20. copper oxyquinolate	*		. x

Example 4B

Composition comprising, percentages by weight to a total of 100%.

	Oomposition and pro-	8,1
5	25-100%	at least one member of the designated terpenoid group
	0%-trace	wetting agents
	0-50%	solvents miscible with water and said member(s) of designated
		terpenoid group
	0-75%	water

5

10

Each of these compositions (4A,B) will typically be used as is though in some cases may be further diluted. If at least medium term (1-4 weeks) protection is desired, then the total weight percentage of members of the designated terpenoid group should be at least 5% (for immersion). Where spray or other application is envisaged, then a level of at least 25% for the members of the designated terpenoid group, should be present. A miscible solvent (which may comprise a number of known solvents) aiding the solubility of the components in water may also be included. However it is sometimes desirable that the members of the designated terpenoid group are present in a separate non-aqueous phase, so that they are more likely to be absorbed by a timber material than run-off or leach from the timber, in water or rain.

Table 5

Presence and lack of inhibition by pine oil and α-terpineol concentrations on four sapstain fungi, FK36, FK63 and FK64.

Chemical	and	Chemical on	Chemical on	Chemical on
Concentration		agar	agar	<u>roof</u>
		Inhibition	Growth on disc	Inhibition
Fungus: FK36				
(Ceratocystis sp.)				
Sterile water		NI	Y	NI
Pine oil 25%		NI	Y	NI
Pine oil 50%		NI	Y	, NI
Pine oil 75%		I	N	I
Pine oil 100%		I	N	I
α-terpineol 25%		NI	Y	NI
α-terpineol 50%		I	N	NI
α-terpineol 75%		İ	N	I
α-terpineol 100%		I	N	I
Copper oxyquinolat	e	I(r)	N	NI

Table 5	Chemical on	Chemical on	Chemical on
continued	agar	agar	<u>roof</u>
	Inhibition	Growth on disc	Inhibition
Fungus: FK48			
(Alternaria sp.)			
Sterile water	NI	Y	NI
Pine oil 25%	NI	Y	NI
Pine oil 50%	NI	Y	NI
Pine oil 75%	I	N	NI
Pine oil 100%	I	N	I
α-terpineol 25%	NI	Y	NI
α-terpineol 50%	NI	N	NI
α-terpineol 75%	I	N	I
α-terpineol 100%	I	N	I
Copper oxyquinolate	I(r)	N	NI
Fungus: FK63			
(Ceratocystis sp.)			
Sterile water	NI	Y	NI
Pine oil 25%	NI	Y	NI
Pine oil 50%	NI	Y	NI
Pine oil 75%	I	N	I
Pine oil 100%	I	N	I
α-terpineol 25%	NI	Y	NI
α-terpineol 50%	NI	Y	NI
α-terpineol 75%	I	N	I
α-terpineol 100%	I	N	I
Copper oxyquinolate	I(r)	N	NI

Table 5	Chemical on	Chemical on	Chemical on
continued	<u>agar</u>	agar	<u>roof</u>
	Inhibition	Growth on disc	Inhibition
Fungus: FK64			
(Ceratocystis sp.)			
Sterile water	NI	Y	NI
Pine oil 25%	NI	Y	NI
Pine oil 50%	VSI	N	NI
Pine oil 75%	I	N	I
Pine oil 100%	I	N	I
α-terpineol 25%	NI	N	NI
α-terpineol 50%	I	N	I
α-terpineol 75%	I	N	I
α-terpineol 100%	· I	N	I ,
Copper oxyguinolate	I(r)	N	

Key

.5

I = inhibition observed

I (r) = inhibition in a definite ring form

NI = no inhibition

VSI = very slight inhibition

Y = yes

N = no

10 Example Five

The next examples are generally intended for spray or fumigant action though may also be diluted for use. They may also find use for immersion and forced impregnation techniques. Some specific formulations for compositions include:

Example 5A

15 Composition comprising, percentages by weight to a total of 100%:

25-100% at least one memb

at least one member of the group of active substances;

0-75% turpentine and/or solvent, other than water, miscible with above

components (when containing above dissolved components) other

than water.

Example 5B

Composition comprising, percentages by weight to a total of 100%:

25-100%

 α -terpineol, thymol, oil of thyme and/or pine oil;

0-75%

5

turpentine and/or solvent, other than water, miscible with above

components (when containing above dissolved components) other

than water.

Example 5C

Composition comprising, percentages by weight to a total of 100%:

25-100%

geranial, neral, 6-pentyl- α -pyrone, and/or furfural;

10 0-75%

turpentine and/or solvent, other than water, miscible with above

components (when containing above dissolved components) other

than water.

Example Six

These compositions are generally suitable for spray application rather than furnigant application (for which Example 5 is generally more suitable). The compositions of Example 6 may also be used for immersion application though may be diluted before such use. Some specific compositions include:

Example 6A

Composition comprising, percentages by weight to a total of 100%.

20 25-75%

at least one member of an active group of compounds

0%-trace

wetting agents

25-75%

water

optional

other diluent/carrier/solvents such as an alcohol

Example 6B

Composition comprising, percentages by weight to a total of 100%:

25-75%

a-terpineol and/or pine oil;

0%-trace

wetting agents

25-75%

water

optional

other diluent/carrier/solvents such as an alcohol

Example 6C

Composition comprising, percentages by weight to a total of 100%:

25-75%

eugenol, resorcinol related diphenols, thymol and/or oil of thyme

0%-trace

wetting agent

5 25-75%

10

20 .

30

water

optional

another diluent/carrier/solvent such as an alcohol

Example Seven

A method for the prevention of sapstain comprising the application of an effective amount of at least one member of the group of active substances. The method may also be directed at, or address in addition, wood degradation and pest control.

The method of application may comprise the use of a composition including the aforesaid active members, which may include (but not necessarily be restricted to) the use of the compositions described in the examples herein.

The method of application may comprise spray application to exposed, and especially non-bark covered, surfaces of timber. Another method which has appeared effective in trials is the use of a pad moistened with a composition and pressed against the cut portion. This may be left against the target area to be absorbed into the timber.

Application by immersion is an alternative. Application by fumigation may also be performed though compositions having relatively high amounts of volatile components, and low levels of water (if not completely absent) will typically be used in such instances. The use of elevated temperatures to increase the volatility of components is also a possibility, and fumigation may be combined with any timber drying or processing step. In reconstituted timber and paper products, the composition may be incorporated during a processing step.

25 The length of any preventative effect will be determined by the quantity of a member(s) of said group of active substances which is administered to the material. The results of Examples 1-3 may be used as a general guideline though some minor experimentation may be required to optimise the effect under different conditions.

For a treatment for freshly felled trees, a suitable composition should be applied to exposed surfaces as soon as possible after felling. Delays of up to 7 days may be acceptable in some cases, depending upon the presence of infectious material at the felling site and climatic conditions.

5

10

15

20

25

30

Example Eight

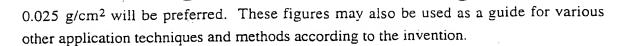
A method of treatment for materials already infected with sapstain, wood degrading organisms and/or pest populations comprises the application of an effective amount of at least one member of the group of active substances. Typically the methods of application are those described in respect of Example 7. Where there is substantial infection by sapstain organisms, the amount of compound(s) administered will generally be higher than for preventative methods and will typically be similar to those for long term prevention of sapstain fungi, decay or pest attack. It is noted that the active components do not appear to be consumed during their fungicidal action and the increased amount is generally due to the fact that in a preventative sense, the active components are merely acting as a barrier to prevent the increase of sapstain or other organisms. However when treating, for instance, sapstain infected wood, it should be noted that most sapstain fungi grow and travel through the parenchyma of the timber. Consequently, if complete eradication of the sapstain fungi is required (which is generally preferable to avoid subsequent attack of commonly associated wood degrading organisms) a higher level of impregnation (though this may be at a relatively low level) would generally be required. Pest attack, especially by beetles, may often penetrate into the wood and thus deeper impregnation of active components into the wood may be desirable for increased protection or to affect pests already present. Immersion techniques will typically be preferred though extended fumigation techniques may also be equally effective. Spray techniques which allow relatively heavy saturation may also be suitable.

Example Nine

In some instances a rudimentary surface application of a suitable composition may be applied in the manner of Example 7. This may be suitable for instances where control of surface visible sapstain growth may merely need be addressed.

However, the formation of a barrier layer over possible infection sites (typically exposed timber) is a method which may be employed on many timbers. This may also include dressed and finished timbers. Typically a barrier layer may only be of up to several mm depth, on average, though timber grain (e.g. the more absorbent end grain) though density may affect the depth of impregnation.

Typically a barrier layer suitable for short to medium term protection will comprise the application of up to $0.05g/cm^2$ in total of one or more members of the group of active compounds (not including diluents, carriers etc.), this value being an average over the coated surface. More preferably, including for economic reasons, application of 0.002-



Example Ten

Tests comparable to example 1 were performed at a timber mill site. The relative results are graphically illustrated in Figures 10 through 13. A key to the samples is in Table 6.

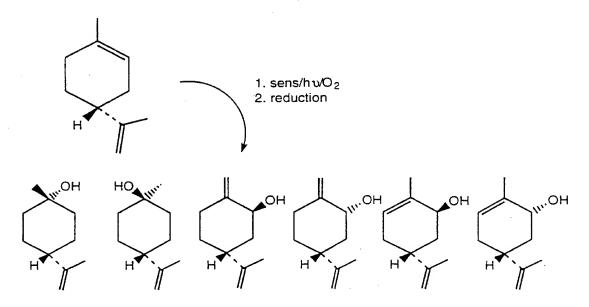
Table 6
The key for the figures 10-13, 17-18:

		-	, , , , , , , , , , , , , , , , , , , ,
	CONT	-	control
	1.02N	-	NUFILM TM + composition containing the compounds of
10	,		Formula 9
	1.02FK	-	composition containing the compounds of Formula 9
	W	-	a composition comprising a mixture of diastereoisomeric
			carveols and allylic alcohols derived from the oxidation of
			limonene
15	WN	· -	NUFILM TM + a composition comprising a mixture of
			diastereoisomeric carveols and allylic alcohols derived from
			the oxidation of limonene
	2. 5 T	<u>.</u> :	25% Ti tree oil
20	10T		100% Ti tree (Malaleuca alternifolia) oil
20		-	
	2.18N	-	NUFILM [™] + composition containing the compounds of Formula 10
	2.18FK	-	composition containing the compounds of Formula 10
	2.5B	-	a composition comprising 25% BC 1000™.
25	HI	-	highlight (chemical) fungicidal
	2.5P	-	25% pine oil
	4.0P	-	40% pine oil
	6.0P	-	60% pine oil
	8.0P	-	80% pine oil
30	10B	,	a composition comprising 100% BC 1000™.
	DIFF	-	DIFFUSOL TM - chemical fungicide
	BBAC	-	Nutrient Broth & Bacteria
,	PBAC	-	Bacteria from Petri Dishes.
	T25	-	25% tea tree (Melaleuca alternifolia) oil
35	T100		100% tee tree (Melaleuca alternifolia) oil

Table 6 continued

	B25	-	a composition comprising 25% BC 1000™.
	B100	-	a composition comprising 100% BC 1000 TM
	P25	-	25% pine oil
5	P40	-	40% pine oil
	P60	-	60% pine oil
	P80	-	80% pine oil
	P100	-	100% pine oil
	TH25	-	25% thyme oil
10	TH100	-	100% thyme oil

Reaction Sequence 8



Range of products from photooxygenation of (+)-limonene

15 Formula 9

5

10

15

Formula 10

It is noted that Tea tree (Malelueca alternifolia) oil used in the trials was sourced from Australia, the typical composition of Australian sourced oils being approximately 30% terpine-4-ol and 15% cineol. The lower percentage of terpenoid compounds is reflected in the generally lesser degree of effectiveness of tea tree oil in the trials. Consequently, where higher levels of activity are required, sources of these terpenoid compounds other than tea tree oil may be preferred, or the levels of terpenoid compounds in the oil increased.

Example Eleven

Another method of application is by injection into an article. It is envisaged that this technique will be used more for larger articles such as trunks and portions thereof though may also be used for infected areas. Typically a probe inserted into the timber (a pilot hole may be formed first) will inject a composition comprising at least one member of group of active compounds. Often this will be under pressure. Typically a liquid will be injected though a gas or vapour under pressure may also be used. This may allow more effective transport of the active components if the timber is damaged or porous due to wood degraders, and pests etc.

20 Example Twelve

Further trials by the applicant investigated the effectiveness of pine oil for addressing sapstain in different species of timber. The procedures followed were similar to the techniques described in Example 1 and gauged the effectiveness of varying concentrations of pine oil in inhibiting sapstain growth on the timber.

Figure 14 graphically illustrates the results of these trials. From these results pine oil appears universally effective for virtually all timbers in respect of sapstain inhibition. Even at 10% the pine oil exhibited a high degree of effectiveness in inhibiting sapstain.

For the eucalypts, and Douglas Fir, where inhibition was not absolute, inhibition was still substantial compared to the control.

The timbers chosen for the trial represent a cross-section of commercially important timbers and include:

5 Red Beech Nothofagus fusca

Liquid Amber Liquidamber styraciflua

Tulip Tree Liriodendron tulipifera

Box Elder Acer negundo

European Ash Fraxinus excelsior

10 European Beech Fagus sylvatica

Gum Tree Eucalyptus fastigata

Alder Alnus glutinosa

Blue Gum Eucalyptus nitens

Monterey Pine Pinus radiata

15 Douglas Fir Pseudotsuga menziesii

White Poplar Populus lava

Examples Thirteen

20

25

Further trial were conducted. In one instance, small wood blocks were treated with dilutions of active pine oil fractions and sapstain fungi. Figure 21 illustrates the results of these trials, where PC530 = synthetic pine oil with 85% terpene alcohols; PC540 = synthetic pine oil with 65% terpene alcohols; PC550 = natural pine oil with 85% terpene alcohols).

A further trial was performed with wood chips – the results are seen in figure 22. PC530, PC540, and PC 550 are as above. PC620 = myrcene 74%; PC560 = dipentene; PC500 = α -pinene.

Further trials were performed at two different mill sites. The key is given in table 7 while the results are illustrated in figures 23 through 27.

Example Fourteen

Further trials were performed to evaluate the effectiveness of pine oil for sapstain control on a variety of wood types. The samples were evaluated after 14, 29 and 50 days, and the results are shown in tables 8-10. A lower score is better

5

Example Fifteen

Tests were performed at a timber mill site in which timber samples were impregnated with various compositions. Wood tablets (90mm x 50mm x 18mm) were cut from freshly sawn timber. The tablets were painted with a painter's brush with 2.5 ml/block of the following emulsion. The relative results are graphically illustrated in Figures 15 and 16. A key to the samples is in Table 6.

Table 7

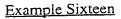
Treatment Code	Treatment
1	FK247 Fungal BCA + alcosorb
*2	FK228 Fungal BCA + alcosorb
*3	100% Pine oil Eka Nobel (PC530)
*4	100% White Thyme oil
*5	Fungicide NP1 (debarked logs)
*7	Control 1
*8	100% Pine oil Eka Nobel (PC540)
*9	100% Pine oil Bronson & Jacobs 💻
10	80% Pine oil Eka Nobel (PC530) ■
11 ·	60% Pine oil Eka Nobel (PC530)
12	40% Pine oil Eka Nobel (PC530)
13	25% Pine oil Eka Nobel (PC530) 💻
14	80% White Thyme oil ■
15	60% White Thyme oil
16	40% White Thyme oil ■
17	25% White Thyme oil ■
18	Fungicide NP1 dip - Kawerau only
19	Diffusol - Tokoroa only
20	100% Litsea cubeba oil =
21	25% Litsea cubeba oil ■
22	25% Pine oil Eka Nobel (PC540) 📱
23	25% Pine oil Bronson & Jacob 💻
24	NP1 spaced - Kawerau only
25	Diffusol spaced - Tokoroa only
26	Control spaced
27	25% Pine oil Eka Nobel (PC530) spaced
28	25% White Thyme oil spaced ■
29	10% Pine oil Eka Nobel (PC530) spaced
30	10% Litsea cubeba oil spaced ■
*31	FK561 Fungal BCA + alcosorb
32	10% White Thyme oil spaced ■

had 0.1% pulse surfactant added at Saw Mills but not to debarked logs NB Fungal BCA's with debarked logs had no alcosorb.

Table 7 continued

Treatment Code	Treatment
33	FK33 Fungal BCA with alcosorb
34	FK75 Fungal BCA with alcosorb
35	FK238 Fungal BCA with alcosorb
36	Control 2
37	NPI - Kawerau only
38	Diffusol - Tokoroa only
39	Alcosorb only
40	100% Litsea cubeba oil + 0.1% pulse surfactant
41	100% Litsea cubeba oil + 0.2% Synthecol Quad BC
42	100% Pine oil Eka Nobel (PC530) + 01% pulse surfactant
43	100% Pine oil Eka Nobel (PC530) + 01% Synthecol Quad BC
44	50% Pine oil Eka Nobel (PC530) + 0.1% pulse surfactant
45	50% Pine oil Eka Nobel (PC530) + 0.2% Synthecol Quad BC
46	α -terpineol + 0.1% pulse surfactant
47	α-terpineol + 0.2% Synthecol Quad BC
48	Fungicide NPI
49	Control 3
50	0.2% Synthecol Quad BC + H ₂ O
51	100% White Thyme oil + 0.1% pulse surfactant
52	100% White Thyme oil + 0.2% Synthecol Quad BC

5



Trials were performed in a manner similar to example 1 to test the efficiency of selected terpenes against *Peniophora gigantea*. The results after 20 days incubation at 25°C are shown in table 11.

Table 8

EFFECTIVENESS OF PINE OIL AS A SAPSTAIN CONTROL ON A VARIETY OF WOOD TYPES AFTER 14 DAYS

PINE OIL %	0	10	25	100
Nothofagus fusca	1.41	0.0	0.0	0.0
Liquidamber styraciflua	0.86	0.0	0.0	0.0
Lirodendron tulipifera	7.6	0.0	0:0	0.0
Acer negundo	2.8	0.0	0.0	0.0
Fraxinus excelsior	1.2	0.0	0.0	0.0
Fagus sylvatica	3.4	0.0	0.0	0.0
Eucalyptus fastigata	4.0	0.0	0.0	0.0
Alnus glutinosa	0.0	0.0	0.0	0.0
Eucalyptus nitens	9.6	1.4	0:0	0.0
Pinus radiata	8.2	0.0	0.0	0.0
Pseudotsuga taxifolia	3.4	0.4	0.0	0.0
Populus alba	6.8	0.0	0.0	0.0

¹ Scores out of 10

10 Example Seventeen

Another embodiment of the invention is the use of a composition for application to wounds and cuts, such as from pruning or storm damage, in trees. While most trees are resistant, when healthy, to many of the organisms responsible for sapstain or wood degradation, there is occasionally a use for a protective composition.

It is envisaged that most such compositions will comprise a gel, paste, thixotropic, or viscous composition which can be applied to the desired area. Fillers, gelling agents etc. are well known and it is envisaged that the art may be relied upon to provide a composition to the desired consistency incorporating one or more active substances.

In some compositions a substance to provide a, typically water resistant, protective barrier may be relied upon. This barrier may be formed through the formation of a skin, and/or toughening or setting of the applied composition. Many substances able to impart

these properties are known - e.g. many paints, adhesives, and coatings into which one or more members of the group of active substances may be included. Many waxy substances, shellacs, epoxies etc. may also find use - see leach retarding substances earlier in the specification. A paste which forms a cap over a wound may be considered.

Table 9: EFFECTIVENESS OF PINE OIL AS A SAPSTAIN CONTROL ON A

VARIETY O	F WOOD TYPE	ES AFTER 2	9 DAYS	
PINE OIL %	0	10	25	100
Nothofagus fusca	7.01	0.0	0.0	0.0
Liquidamber styraciflua	9.4	0.0	0.0	0.0
Lirodendron tulipifera	9.2	0.0	0.0	0.0
Acer negundo	5.2	0.0	0.0	0.0
Fraxinus excelsior	5.8	0.0	0.0	0.0
Fagus sylvatica	5.8	0.0	0.0	0.0
Eucalyptus fastigata	6.6	0.0	0.0	0.0
Alnus glutinosa	0.6	0.0	0.0	0.0
Eucalyptus nitens	6.0	1.8	0.0	0.0
Pinus radiata	9.4	0.0	0.0	0.0
Pseudotsuga taxifolia	5.2	1.8	0.0	0.0
Populus alba	10.0	0.0	0.0	0.0

1 Scores out of 10

TABLE 10: EFFECTIVENESS OF PINE OIL AS A SAPSTAIN CONTROL ON A VARIETY OF WOOD TYPES AFTER 50 DAYS

10 10 25 100 PINE OIL % 0 10.010.0 0.0 0.0 Nothofagus fusca 1.6 0.0 0.0 Liquidamber styraciflua 9.6 0.0 0.0 0.0 10.0 Lirodendron tulipifera 0.0 10.0 0.0 0.0 Acer negundo 0.0 0.0 0.0 5.8 Fraxinus excelsior 0.4 0.0 0.0 Fagus sylvatica 10.0 0.0 0.0 0.0 7.0 Eucalyptus fastigata 0.0 0.0 0.0 0.8 Alnus glutinosa 3.0 0.0 0.0 7.0 Eucalyptus nitens 0.0 0.0 0.0 10.0 Pinus radiata 3.0 0.0 0.0 6.0 Pseudotsuga taxifolia 0.0 0.0 0.4 Populus alba 10.0



Treatment	100%	50%	24%	10%
1	Т	- .	-	-
2	T	т	Т	-
3	Т	-	-	-
4	Т		-	-
5	· -	-	· -	-
6		-	,	-
7	-	-	-	-
8		-	-	-
9	N/A	N/A	Т	-
10	Т	-		

Treatments: (Tables 8-11)

- 1. Thyme oil red
- 5 2. Eugenol BP
 - 3. Nerol 900
 - 4. alpha-Terpineol
 - 5. Terpinyl acetate
 - 6. alpha-pinene
- 10 7. Dipentene
 - 8. Spearmint oil
 - 9. Carvacrol
 - 10. Pine oil 530

T = Total inhibition of fungal growth

N/A = Not enough compound available for these concentrations

- = No inhibition of fungal growth

PESTICIDAL ASPECTS

15 Example Eighteen

Experimental plots were coated with a range of compositions as identified in Table 6. The number of invertebrates observed at each experimental plot were recorded, and have been represented in the graph of Figure 17 which presents an indication of relevant insect populations (and therefore an indication of pest repellence). As can be seen, the pine oil and thyme oil treatments were especially effective though the higher concentrations of

20

5

15

20

25

Teatree oil also exhibited an improvement over the control

The number of different invertebrate species observed at each plot was also recorded and graphically represented in Figure 18.

BC 1000TM is a successor to DF 100TM, which is a phytopharmaco comprising a grapefruit seed extract exhibiting antimicrobial and antifungal properties. DF 100TM is available from CHEMIE BRASILIERA IND. E COM. LTDA., of Sao Jose Dos Campos, Brazil.

A further set of trials were performed at the mill site. The results of these trials are in Figures 19 and 20.

10 Example Nineteen

A method for treating exposed timber susceptible to insect and pest attack by the spray application of a composition comprising at least 25% pine oil or thyme oil or selected active control agents normally present therein. A spray coating over exposed and vulnerable surfaces is applied so as to form a surface barrier layer of timber impregnated with said composition. This may be applied to exposed timber on newly felled, or pruned, trees.

Example Twenty

Alternatively, articles to be treated, which may already support pest infestations, are immersed in a composition comprising at least 0.1% of a selected active agent. The selected active agent may be present in the form of an essential oil, extruded oil plant extract or the like. Often levels of the selected active agents will be at least 0.5-5% with higher concentrations being used in techniques employing short immersion times.

Immersion techniques will typically provide greater impregnation of active ingredients in compositions. Impregnation can be controlled by immersion times and composition concentrations, as well as by other factors. Methods such as described in examples 5-7, 11 and 13 may be relied upon.

Example Twenty One

Insect repellent and controlling properties may also be provided by the introduction of a selected control agent by a fumigation type technique.

Standard fumigation techniques may be used though it is also envisaged that techniques performed at elevated temperatures and pressures other than atmospheric may be employed. Reduced atmospheric pressures may increase the volatility of certain compounds, resulting in an increase in their mobility. Conversely, increased pressures

may provide for greater impregnation, especially in near satura. Atmospheres. Many combined vacuum/pressure techniques are known in the art.

Example Twenty Two

5

10

20

A barrier resulting from the administration/application of a selected control agent or suitable composition, to the surface of an article is created. Typically a barrier layer suitable for short to medium term protection or to control many pests present, will comprise the application of up to 0.05g/cm^2 in total of one or more members of the designated terpenoid group, and/or group of active agents (not including diluents, carriers etc.), this value being an average over the coated surface. More preferably, including for economic reasons, application of $0.002\text{-}0.025 \text{ g/cm}^2$ is applied for a relatively active compound such as the terpenoids. These figures may also be used as a guide for various other application techniques and methods according to the invention. Values outside of these ranges may be considered and employed.

Examples Twenty Three

The use of an effective amount of a selected active control agent, or composition containing same, as a pesticide applied to crops or pasture to prevent and/or address pest problems.

At least one selected active agent, or composition containing same, incorporated into an article during its manufacture to act as a pest repellent and/or address potential pest problems.

A spray aerosol capable of dispersing a selected active agent, or composition containing same. Typical uses include as a pest repellent and/or pesticide.

MEDIUM TO LONG TERM PRESERVATION

Example 24A

Composition comprising, percentages by weight to a total of 100%.

0.5-100%

at least one member of group of active substances

0%-trace

a wetting agent

0-99.5%

organic solvent immiscible, or only partially miscible with water.

Example 24B

30 Composition comprising, percentages by weight to a total of 100%.

0.5-100%

at least one member of group of active substances

0%-trace

a wetting agent

0-99.5%

water.

Example 24C

Composition comprising, percentages by weight to a total of 100%.

0.5-100%

at least one member of group of active substances

0%-trace

a wetting agent

5 0-95%

solvent miscible with water and said member(s) of designated

terpenoid group

0-95%

water

Example 24D

Composition comprising, percentages by weight to a total of 100%.

10 5-40%

at least one member of group of active substances

0%-trace

a wetting agent

0-50%

solvent miscible with water and said member(s) of designated

terpenoid group

0-75%

water

Each of these compositions will typically be used as is though in some cases may be diluted. It is envisaged that immersion will be the preferred method of application, and forced conditions may be applied. Other methods of impregnation may also be performed.

Where spray or other application is envisaged, then a higher level of active substances, should be present. Typically this will be 40% or greater, though repeat or highly saturated (i.e. thoroughly wetting the article) spray application may make more diluted compositions more practicable.

A miscible solvent (which may comprise a number of known solvents) aiding the solubility of the components in water may also be included. However it is sometimes desirable that chosen active substances are present in a separate non-aqueous phase – see example 25.

Example Twenty Five

These compositions predominantly contain two solvent phases. They may also include a loss reducing agent which will normally, but not necessarily, be present in a single phase. Loss reducing agents in both phases may also be employed.

25

30

Example 25A

Composition comprising, percentages by weight to a total of 100%.

0.5-75% at least one member of group of active substances

0%-trace a wetting agent

5 0-90% organic solvent immiscible, or only partially miscible with second

carrier.

0-90% Second carrier or solvent, which may be water.

Example 25B

Composition comprising, percentages by weight to a total of 100%.

10 0.5-75% at least one member of group of active substances

0%-trace a wetting agent

0-90% organic solvent immiscible, or only partially miscible with second

carrier.

0-90% Second carrier or solvent, which may be water.

15 0.1-25% Loss controlling agent

Example 25C

Composition comprising, percentages by weight to a total of 100%.

0.5-75% at least one member of group of active substances

0%-trace a wetting agent

20 0-90% first solvent immiscible, or only partially miscible with second

carrier/solvent.

0-90% Second carrier or solvent, which may be water.

0.1-25% Loss controlling agent(s) miscible with either first or second

carrier/solvent

25 Example 25D

Composition comprising, percentages by weight to a total of 100%.

0.5-75% at least one member of group of active substances

0%-trace a wetting agent

0-90% first solvent immiscible, or only partially miscible with second

30 carrier/solvent.

0-90% Second carrier or solvent, which may be water.

0.1-25% Loss controlling agent(s) miscible with either first carrier/solvent

0.1-25% Loss controlling agent(s) miscible with either first carrier/solvent

The loss controlling agents may comprise a range of different substances which may act as a barrier to reduce loss of chosen active substances (see also previously within this specification). Higher molecular weight, naturally occurring compounds may be considered. These may be derived from timber or plant matter, but may also be sourced elsewhere.

Example Twenty Six

The next examples are generally envisaged for spray or fumigant type application. Some specific formulations for compositions include:

Example 26A

10 Composition comprising, percentages by weight to a total of 100%.

25-100%

at least one member of group of active substances;

0-75%

5

turpentine or solvent, other than water, miscible with above

components (when containing above dissolved components).

Example 26B

15 Composition comprising, percentages by weight to a total of 100%.

25-100%

 α -terpineol, thymol, pine oil, and/or oil of thyme;

0-75%

turpentine or solvent, other than water, miscible with above

components (when containing above dissolved components).

Example 26C

20 Composition comprising, percentages by weight to a total of 100%.

25-75%

at least one member of a designated terpenoid group

0%-trace

wetting agent

25-75%

water

optional

another diluent/carrier/solvent such as an alcohol

25 Example 26D

Composition comprising, percentages by weight to a total of 100%.

25-75%

α-terpineol, thymol, pine oil and/or oil of thyme

0%-trace

wetting agent

25-75%

water

30 optional

another diluent/carrier/solvent such as an alcohol

Example Twenty Seven

A method for inferring preservative properties to timber and other materials comprising the administration of an effective amount of at least one member of group of active substances.

The method of application may comprise the use of a composition comprising at least one member of group of active substances, which may include (but not necessarily be restricted to) the use of the compositions described in the examples herein.

Immersion of the article in a bath exceeding 30°C is preferred. Higher temperatures, in excess of 50°C may be used if the integrity of the timber or article is not compromised.

The length of any preventative effect will be determined by a number or factors, including the required depth of penetration, the nature of the solvents and composition, and the porosity and density of the timber or article. The guidelines indicated in example 28 may be followed.

Example Twenty Eight

A fumigant type application method where a saturated or near saturated atmosphere is present. This will generally be sufficient to ensure wetting and penetration into the timber or article.

Commonly elevated temperatures will be used to increase the volatility of chosen active substances and solvents. Water may, but will generally not be, used as a carrier but may be present for other reasons. Pressurisation to several atmospheres or greater may also be considered.

Example Twenty Nine

20

25

30 -

Most methods will not result in total impregnation of an article but result in a barrier comprising impregnated preservative agents from outside surfaces inwards. This will generally follow a decreasing gradient, though generally the probability of attack also decreases inwardly.

Typically a barrier layer suitable for short to medium term protection will comprise the application of in excess 0.05g/cm^2 in total of chosen active substances (not including diluents, carriers etc.). Typically this value is the average level of preservative agent present on the region comprising from the surface and up to 0.5 mm depth.

The required depth of penetration required will vary. For dense timbers, a lesser depth of impregnation may be required. As a guide, typical 125mm Pinus radiata round posts

would have an impregnation depth of at least 5mm, and preferably 10mm or greater. The impregnation depth being the distance from the surface to the depth where the level of chosen active substances is 2.5% of the value present between the surface and 0.5mm depth. Typically an impregnation depth of at least 5mm will be suitable for most non-hardwood timbers, though 10mm is preferred and for more porous or susceptible timbers, greater depths or near total impregnation may be preferred.

Another guide for application is the amount of chosen active substance(s) applied to the surface. This may be a better guide for spray and fumigant type application methods. By way of example, application of in excess of $0.025~g/cm^2$ (total chosen active substances) to the surface will be preferred. More preferably, the figure will exceed $0.05~g/cm^2$. These values are for compounds exhibiting activities similar to the terpineols, and may need to be adjusted for compounds have significantly lesser or greater activities.

A final guide is to base the amount of chosen active substances on the weight of the article. For most timbers, chosen active substances exceeding 0.03% by weight of the article may be applied. More preferably, this will exceed 0.12% by weight. However it is noted that the surface area, rather than weight, will provide a better guide for calculating quantities required.

These figures may also be used as a guide for various other application techniques and methods according to the invention.

20 Example Thirty

5

10

15

25

A method for inferring preservative properties to timber comprising immersing said timber in a bath comprising α -terpineol, thymol, pine oil, and/or oil of thyme. Up to 60% by weight of a miscible solvent may be included. The bath may be reconstituted to replace lost components after each batch. The bath is maintained at 20-50°C and the timber immersed until an impregnation depth of at least 5 mm (or less depending on the thickness of the article) from each exterior surface is achieved. For long term preservation, this impregnation depth may be increased to 10mm or the degree of saturation (by chosen active substances) increased to at least 40% of the surface-0.5mm average value at a depth of 5mm.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

THE CLAIMS DEFINING THE INVENTION ARE:

- 1. A method for addressing at least one of wood degradation, sapstain and pests, in wood or wood based materials comprising the incorporation or application to the wood or wood based material of a composition comprising at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:

Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyl, alkenyl$

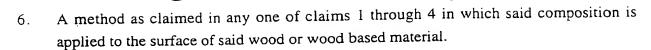
 $R_2 = H$

 $R_3 = OH$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

- 2. A method as claimed in claim 1 in which said terpene derivatives comprise: α -terpineol, α -terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, hydroxy-citronellal, terpinen-4-ol, pulegol, isopulegol, β -terpineol, γ -terpineol, nerol, δ -terpineol, and said β -unsaturated aldehydes and ketones comprise: geranial, neral, furfural, and ionone, pulegone, isopulegone, carrone, verbenone, myrtenal, perillaldehyde, and piperitone.
- 3. A method as claimed in claim 1 in which chosen members, for application, of the group of active substances are naturally occurring within timber, or derivatives of compounds naturally occurring within timber.
- 4. A method as claimed in claim 3 in which the chosen members are naturally occurring within, or a derivative of substances naturally occurring within, the wood being, or present within the material being, treated.
- 5. A method as claimed in any one of claims 1 through 4 in which the wood or wood based material is impregnated with a composition including at least one active substance.



- 7. A method as claimed in any one of claims 1 through 4 in which said composition is water based
- 8. A method as claimed in any one of claims 1 through 4 in which the composition is applied to freshly exposed faces of the wood or wood based material.
- 9. A method as claimed in any one of claims 1 through 5 which also includes the application to the wood or wood based material of a fungicidal or pesticidal agent, other than members of the group of active substances.
- 10. A method for conferring medium to long-term protection to wood and wood-based materials against at least one of pests and organisms responsible for either or both sapstain and wood degradation, said method comprising the impregnation into said timber or timber-based material of at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:

Where:

 $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR:

 $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

Phenolic Compound

R₁

OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

 $R_3 = OH$

11. A method as claimed in claim 10 in which said terpene derivatives comprise: α-terpineol, α-terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, hydroxy-citronellal, terpinen-4-ol, pulegol, isopulegol, β-terpineol, γ-terpineol, nerol, δ-terpineol, or in which said β-unsaturated aldehydes and ketones comprise: geranial, neral, furfural, ionone, pulegone, isopulegone, carrone, verbenone, myrtenal, perillaldehyde, and piperitone.

12. A method as claimed in craim 10 in which a said active composition is introduced into a wood-based material during its manufacture.

- 13. A method as claimed in claim 10 in which the chosen member(s), for application, of the group of active substances is naturally occurring within wood, or derivatives of compounds naturally occurring within wood.
- 14. A method as claimed in claim 13 in which the chosen member(s) is naturally occurring within, or a derivative of substances naturally occurring within, the wood being, or a wood present within the material being, treated.
- 15. A method as claimed in any one of claims 10 through 14 in which at least one chosen member is hydrophobic or has little appreciable water solubility.
- 16. A method as claimed in any one of claims 10 through 14 comprising the use of at least one chosen member which is resistant to leaching from the wood or wood based material.
- 17. A method as claimed in any one of claims 10 through 14 in which said active substance(s) are applied by a method comprising at least one of the following steps:
 - prolonged immersion in the chosen active substance(s) or a composition containing same;
 - contact with said chosen active substance(s) under an elevated temperature;
 - contact with said chosen active substance(s) under greater than atmospheric pressure;
- 18. A method as claimed in any one of claims 10 through 14 in which an applied active substance is substantially within a gaseous or vaporised state for application.
- 19. A method as claimed in any one of claims 10 through 14 including a step comprising the application of one or more substances limiting the subsequent leaching of the applied active substances.
- 20. A method as claimed in claim 19 in which said substances limiting leaching comprise: shellacs, epoxy materials, oily substances, hydrophobic substances, and waxy substances.
- 21. A method as claimed in any one of claims 10 through 14 including the application of a preservative or insecticidal agent other than the specified active substances.





- 22. A method as claimed in any one of claims 10 through 14 in which sufficient chosen active substance(s) are applied to said wood or wood based material to satisfy at least one of the following criteria:
 - at least, on average, 0.01g of active substance(s) per cm² of treated surface area;
 - at least 0.5% by weight of active substance(s) compared to the weight of timber or timber based material being treated.
- 23. A method as claimed in any one of claims 10 through 14 which includes the use of at least one of a solvent, carrier, emulsifier and wetting agent to increase permeation of a chosen active substance(s) into the timber or timber based material.
- 24. A method of conferring short to medium term control of at least one pest, sapstain and/or wood degrading organism in freshly felled or milled timber comprising the surface application to at least freshly exposed faces of a composition comprising at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:

Ri

Where:

 $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR:

 $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

Phenolic Compound

OR:

 $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

- 25. A method as claimed in claim 24 in which said terpene derivatives comprise: α-terpineol. α-terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, and hydroxy-citronellal, terpinen-4-ol, pulegol, isopulegol, β-terpineol, γ-terpineol, nerol, δ-terpineol.
- 26. A method as claimed in claim 24 in which said β-unsaturated aldehydes and ketones comprise: geranial, neral, furfural, ionone, pulegone, isopulegone, carrone, verbenone, myrtenal, perillaldehyde, and piperitone.

27. A method as claimed in earm 24 in which the chosen members thaturally occurring within, or a derivative of substances naturally occurring within, the timber being treated.

- 28. A method as claimed in any one of claims 24 through 27 in which the chosen active substance(s) are applied as part of a water based composition or emulsion.
- 29. A method as claimed in any one of claims 24 through 27 in which the chosen active substance(s) are applied by spray.
- 30. A method as claimed in any one of claims 24 through 27 which includes, in addition to the chosen active substance(s), at least one fungicidal or insecticidal agent.
- A method for addressing at least one of wood degradation, sapstain and pests, in wood comprising the administration to the wood of at least one substance occurring naturally within timber of the genus, said substance(s) being members of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:

R₁
OR₂

Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

R₃ = alkyl, aryl, alkoxy

OR: $R_1 = alkyl, alkenyl$

 $R_2 = H$

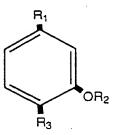
 $R_3 = OH$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$



- 32. A method of treating cutting and pruning wounds on trees and plants comprising the application of a composition comprising at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:



Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

- 33. A method as claimed in claim 32 in which the composition is a paste.
- 34. A method as claimed in claim 32 in which the composition provides a protective layer for the wound or cut.
- 35. A method as claimed in claim 34 in which the composition sets to provide a hardened or toughened surface.

- 36. A composition for addressing at least one of wood degradation, sapstain and pests in wood and wood-based products comprising at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:

Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

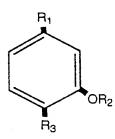
OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

- 37. A composition as claimed in claim 36 in which said terpene derivatives comprise: α-terpineol, α-terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, hydroxy-citronellal, terpinen-4-ol, pulegol, isopulegol, β-terpineol, γ-terpineol, nerol and δ-terpineol.
- 38. A composition as claimed in claim 36 in which said β-unsaturated aldehydes and ketones comprise: geranial, neral, furfural, ionone, pulegone, isopulegone, carrone, verbenone, myrtenal, perillaldehyde, and piperitone.
- 39. A composition as claimed in claim 36 in which the chosen member(s), for application, of the group of active substances is naturally occurring within timber, or derivatives of compounds naturally occurring within timber.
- 40. A composition as claimed in claim 36 in which the chosen member(s) is naturally occurring within, or a derivative of substances naturally occurring within, the wood to be, or a wood present within the material to be, treated.
- 41. A composition as claimed in any one of claims 36 through 40 as an aqueous based suspension, emulsion, or composition.

- 42. A composition as claimed in any one of claims 36 through 40 which includes at least one of: a surfactant, a fungicide, an insecticide; none of which are specified active substances.
- 43. A composition as claimed in any one of claims 36 through 40 which includes a substance which is at least one of hydrophobic, lipophilic, oily, waxy, and capable of displacing water.
- 44. A composition as claimed in any one of claims 36 through 40 in which a chosen active substance exhibits an affinity for wood and is resistant to leaching by water therefrom.
- 45. A composition as claimed in any one of claims 36 through 40 containing at least 0.5% by volume, in total, of chosen active substance(s).
- 46. A composition as claimed in any one of claims 36 through 40 which includes a non-aqueous solvent.
- 47. A composition as claimed in any one of claims 36 through 40 which is sufficiently fluid for spray application.
- 48. A composition as claimed in any one of claims 36 through 40 in the form of a paste.
- 49. A composition as claimed in any one of claims 36 through 40 in which the chosen active substances are present as part of a natural plant-derived extract.
- 50. A composition as claimed in claim 49 in which a natural plant-derived extract is a member of a group comprising: pine oil, thyme oil, and tea-tree (Maleleuca alternifolia) oil.
- 51. A composition as claimed in any one of claims 36 through 40 which includes a substance limiting leaching of chosen active substances.
- 52. A composition as claimed in claim 51 in which said leach limiting substance comprises at least one of: a shellac, an epoxy material, an oily substance, a hydrophobic substance, a waxy substance, and a substance forming a skin on exposure to air.

- 53. A composition having an adverse effect upon one or more organisms of a group comprising pests affecting wood and wood-based materials, and sapstain responsible and wood degrading organisms, said composition including at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:



Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyi, alkenyl$

 $R_2 = H$

 $R_3 = OH$

OR: $R_1 = alkyl, alkenyl$

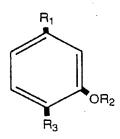
 $R_2 = CH_3$

 $R_3 = OH$

said composition including a suitable carrier for the application of the composition to wood and wood based products.

- 54. A composition as claimed in claim 53 in which said terpene derivatives comprise: α-terpineol, α-terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, hydroxy-citronellal, terpinen-4-ol, pulegol, isopulegol, β-terpineol, γ-terpineol, nerol, and δ-terpineol.
- 55. A composition as claimed in claim 53 in which said β-unsaturated aldehydes and ketones comprise: geranial, neral, furfural, ionone, pulegone, isopulegone, carrone, verbenone, myrtenal, perillaldehyde, and piperitone.
- 56. A composition as claimed in any one of claims 53 through 55 which includes at least one of: a surfactant, a fungicide, an insecticide; none of which are specified active substances.

- 57. A composition for addressing either or both sapstain and wood degradation in timber, said composition including at least one member of a group of active substances comprising:
 - terpene derivatives derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula:



Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

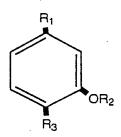
OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

 $R_3 = OH$

and wherein a said chosen active substance occurs naturally within wood of the genus.

- 58. A composition for use in coating wounds and cuts in trees and plants, said composition capable of forming a protective barrier over the area to which it is applied, and including at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;
 - disubstituted mono-phenols, and mono-substituted diphenols of the general formula



Phenolic Compound

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$

59. A composition as claim on claim 58 which is a paste or gel-like consistency.

- 60. A composition as claimed in either claim 58 or claim 59 which forms a hard or tough skin after application.
- 61. A composition as claimed in claim 60 which includes at least one of the following: a shellac, an epoxy material, an oily substance, a hydrophobic substance, a waxy substance, and a substance forming a skin on exposure to air.
- 62. A preservative composition for wood and wood-based materials comprising at least one member of a group of active substances comprising:
 - terpene derivatives such as derivable by the chemical- or bio- technology processing of α and β pinene;
 - β- unsaturated aldehydes and ketones;

Phenolic Compound

- disubstituted mono-phenols, and mono-substituted diphenols of the general formula:

Where: $R_1 = alkyl, aryl, alkoxy$

 $R_2 = H$

 $R_3 = alkyl, aryl, alkoxy$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = H$

 $R_3 = OH$

OR: $R_1 = alkyl, alkenyl$

 $R_2 = CH_3$ $R_3 = OH$

and wherein at least one chosen active substance is resistant to leaching, by water, from timber to which it is applied.

- 63. A composition as claimed in claim 62 which includes a non-aqueous solvent carrier.
- 64. A composition as claimed in claim 62 in which a chosen active substance comprises at least one of α-terpineol, α-terpineol acetate, linalool, citral, geranial, neral, geraniol, citronellol, citronellal, and hydroxy-citronellal, furfural, ionone, pine oil, and tea tree (Melaleuca alternifolia) oil, terpinen-4-ol, pulegol, isopulegol, β-terpineol, γ-terpineol, nerol, δ-terpineol, pulegone, isopulegone, carrone, verbenone, myrtenal, perillaldehyde, and piperitone.
- 65. A composition as claimed in any one of claims 62 through 64 which includes a skin or barrier layer to resist leaching, by water, of chosen active substances.

- 66. A composition as claimed in claim 65 in which said substances limiting leaching comprise: shellacs, epoxy materials, oily substances, hydrophobic substances, and waxy substances.
- 67. Wood, or wood based materials, treated according to a method as claimed in any one of claims 1 through 35.
- 68. Wood, or wood based materials, treated with a composition as claimed in any one of claims 35 through 66.
- 69. A method of addressing at least one of pests affecting wood and wood-based materials, sapstain and wood degradation in wood or wood based materials, substantially as described herein with reference to the accompanying diagrams and contained examples.
- 70. A method for addressing or controlling at least one of pests, and organisms responsible for either or both sapstain and wood degradation, substantially as described herein with reference to the accompanying diagrams and contained examples.
- 71. A method of timber preservation substantially as described herein with reference to the accompanying diagrams and contained examples.
- 72. A composition for at least one of:
 - addressing or controlling organisms responsible for either or both sapstain and wood degradation;
 - addressing either or both sapstain and wood degradation in timber or timber based materials;
 - addressing pests affecting wood and wood based materials, and
 - timber preservation,

substantially as described herein with reference to the accompanying diagrams and contained examples.

Figure 1

GROWTH RATE OF SAPSTAIN FUNGI ON WOOD BLOCKS UNDER CONTROLLED CONDITIONS

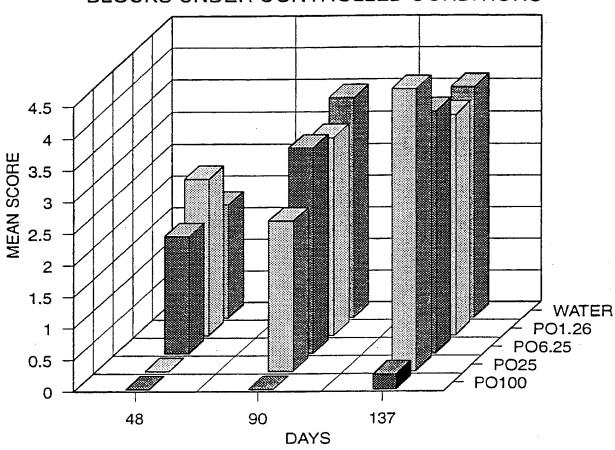


Figure 2

GROWTH OF SAPSTAIN FUNGI ON WOOD BLOCKS UNDER CONTROLLED CONDITIONS AT 48 DAYS

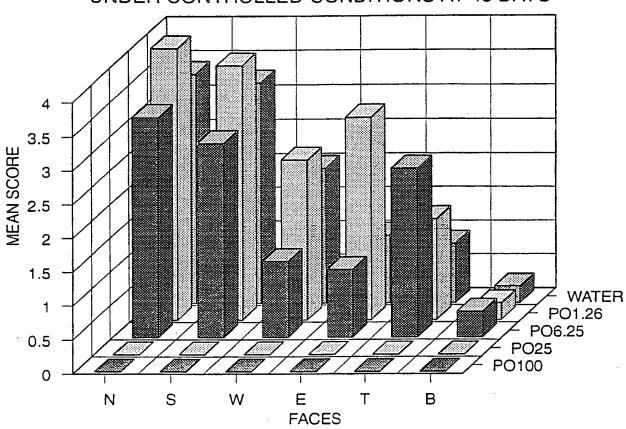


Figure 3

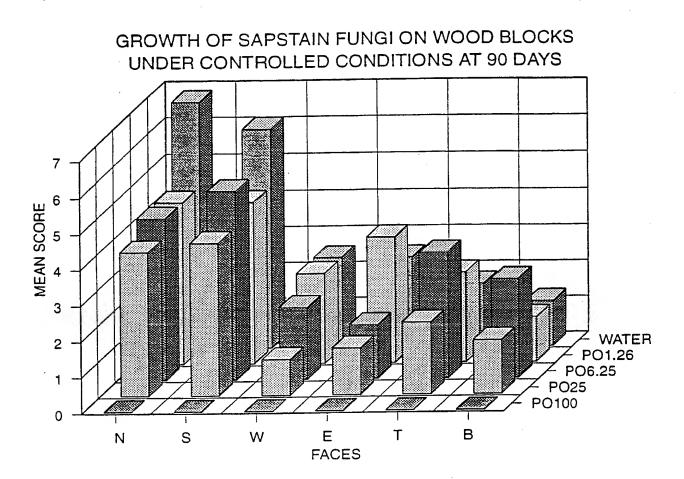


Figure 4

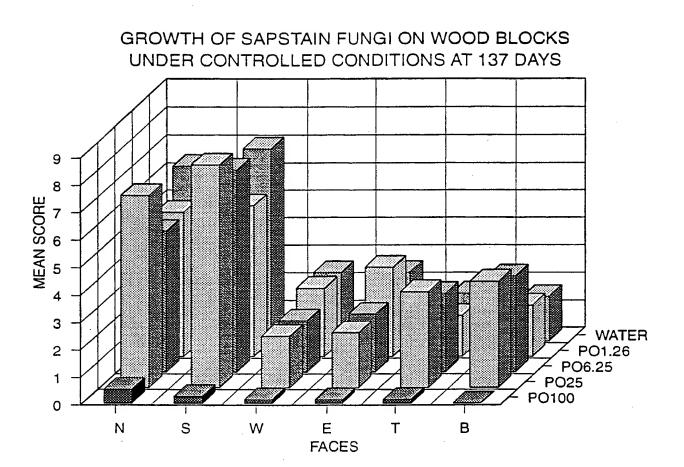
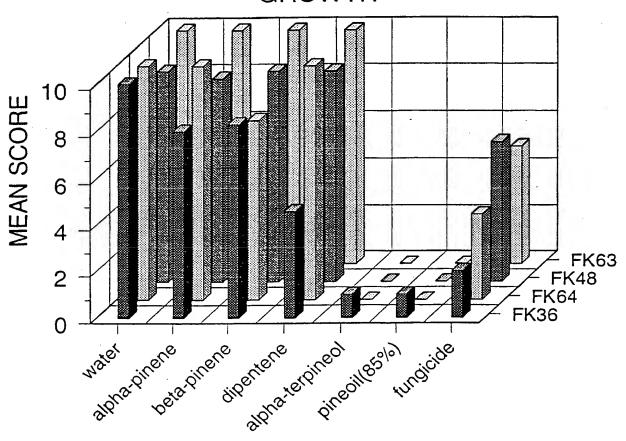


Figure 5

EFFECTS OF VARIOUS TREATMENTS ON FUNGAL GROWTH



TREATMENTS

Figure 6

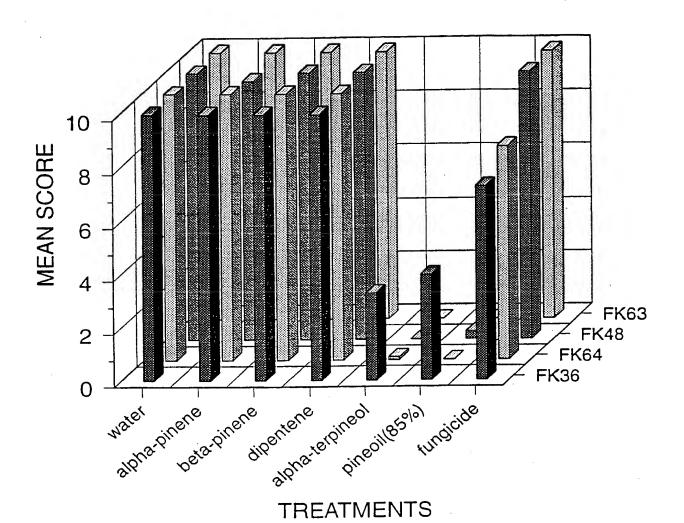
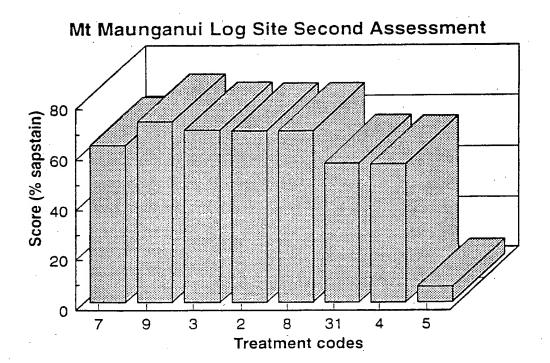


Figure 27



24/24

Figure 25

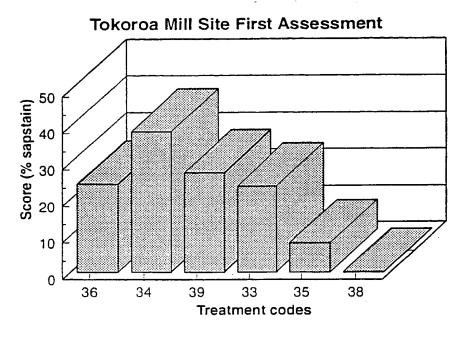


Figure 26

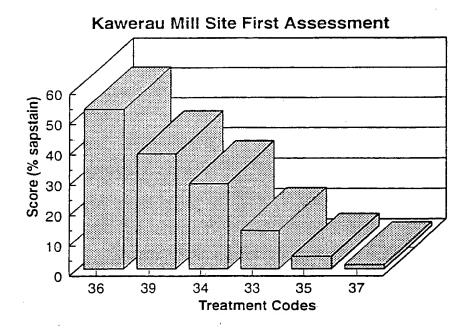


Figure 23

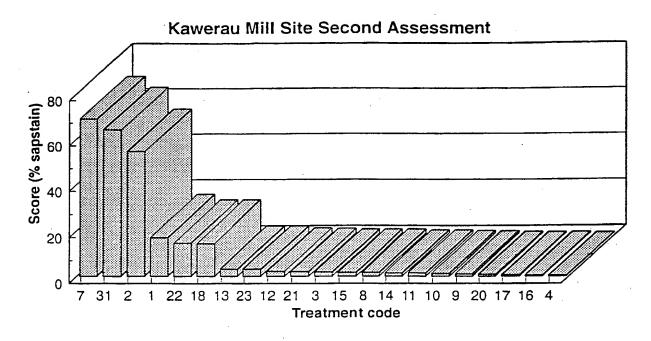


Figure 24

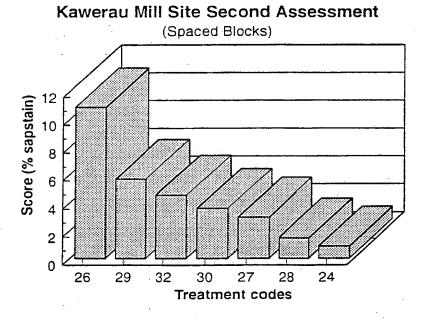


Figure 22



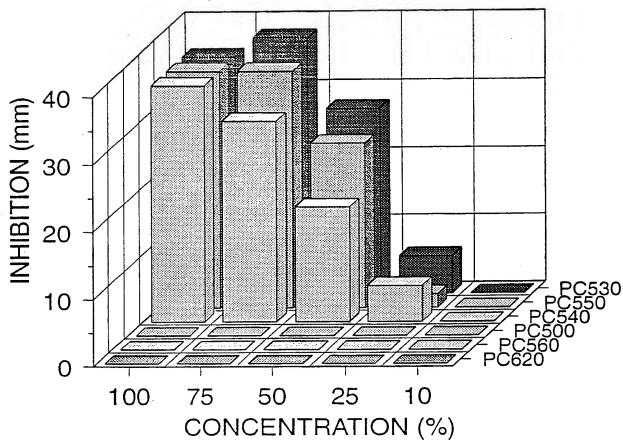


Figure 21

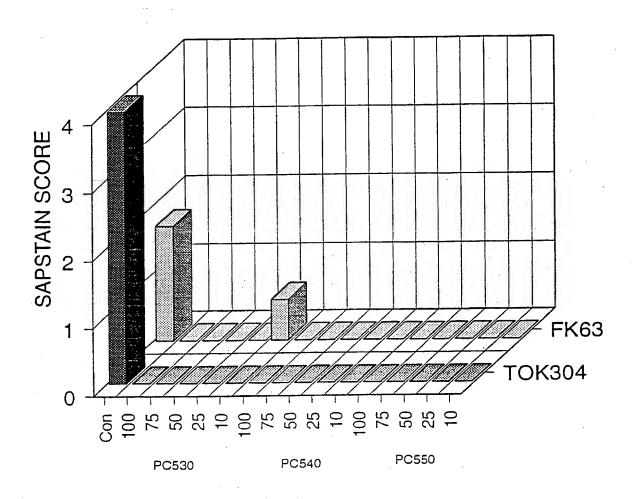


Figure 19

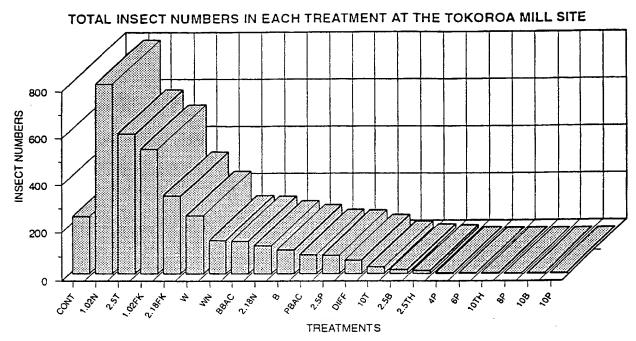


Figure 20

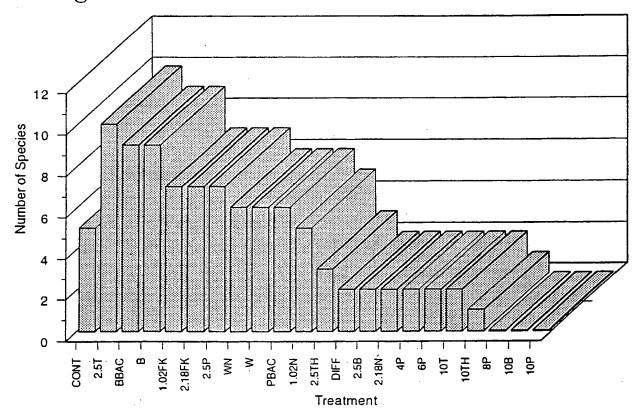


Figure 18

INVERTEBRATES ASSOCIATED WITH SAPSTAIN TREATMENTS (KAWERAU)

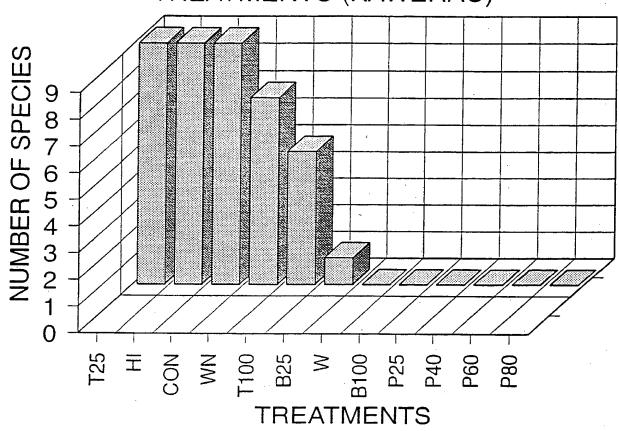


Figure 17

INVERTEBRATES ASSOCIATED WITH SAPSTAIN TREATMENTS (KAWERAU) 160 120 80 40 Total Insects Slugs

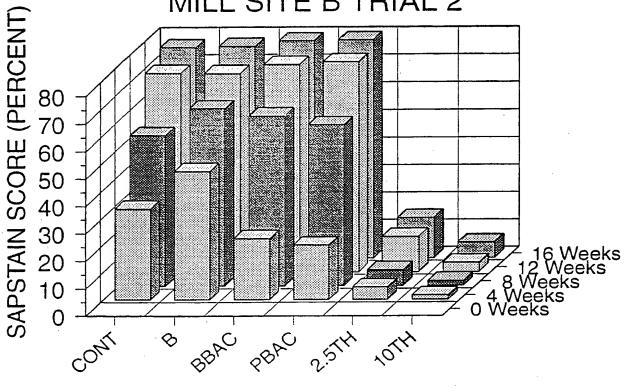
17/24

TREATMENTS

NUMBER OBSERVED PER EXPERIMENTAL PLOT

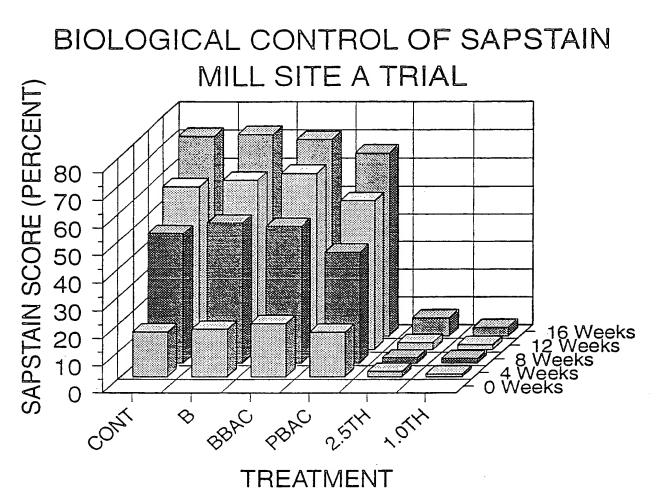
Figure 16

BIOLOGICAL CONTROL OF SAPSTAIN MILL SITE B TRIAL 2

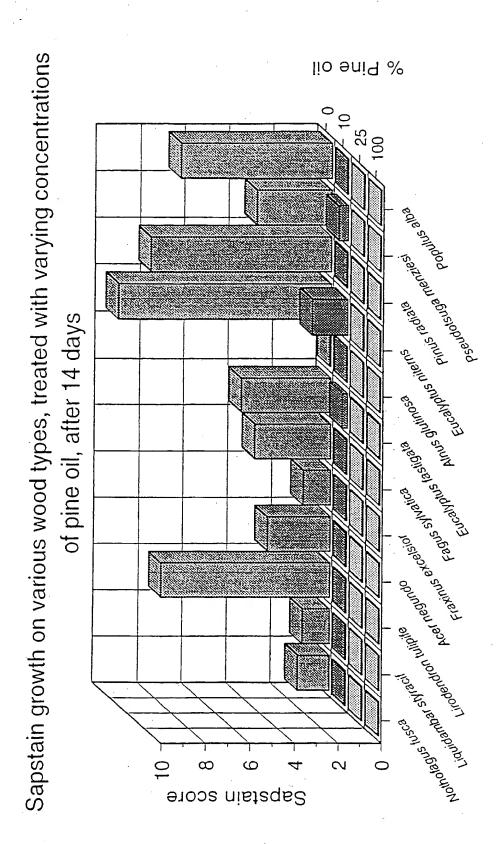


TREATMENT

Figure 15







14/24 SUBSTITUTE SHEET

50

40

30

20

 \Box

Figure 13

BIOLOGICAL CONTROL OF SAPSTAIN EBTRIAL 2 SAPSTAIN SCORE (PERCENT) 80 70 60

13/24

TREATMENTS

Figure 12

BIOLOGICAL CONTROL OF SAPSTAIN MILL SITE B TRIAL 1

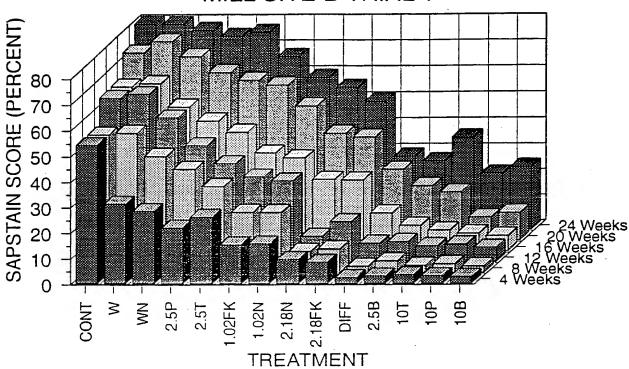


Figure 11

BIOLOGICAL CONTROL OF SAPSTAIN MILL SITE A TRIAL 2

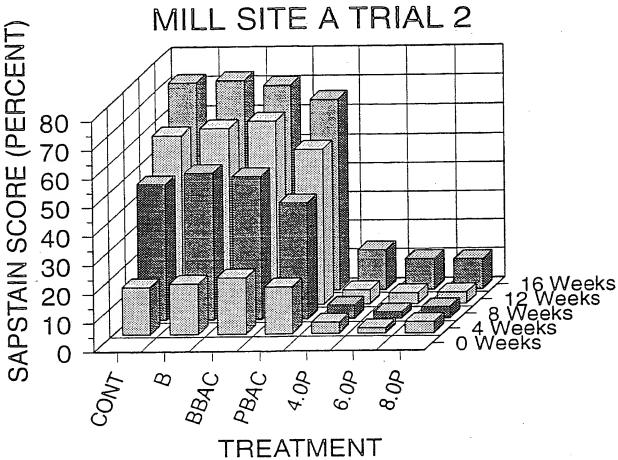


Figure 10

BIOLOGICAL CONTROL OF SAPSTAIN MILL SITE A TRIAL 1

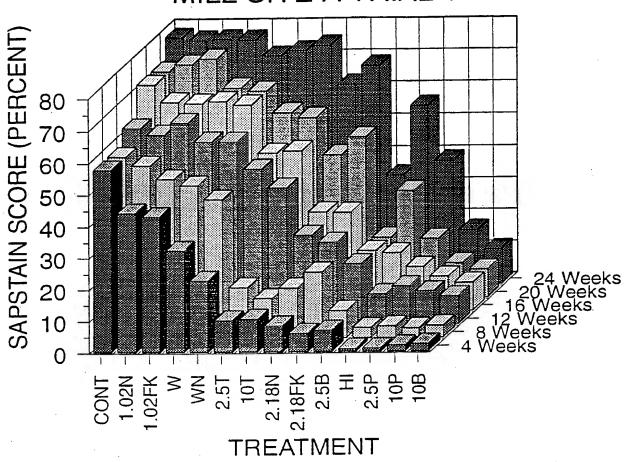


Figure 9

FUMIGATION EFFECTS OF VARIOUS TREATMENTS ON FUNGAL GROWTH

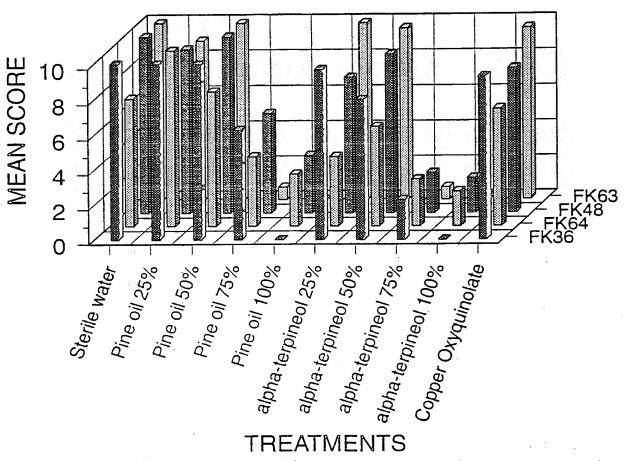
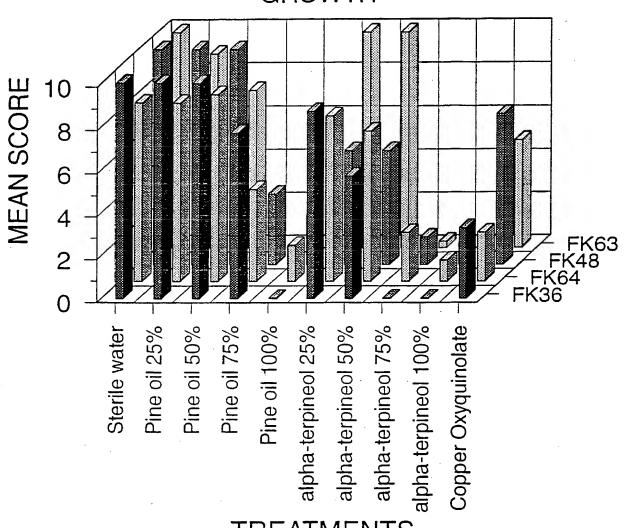




Figure 8

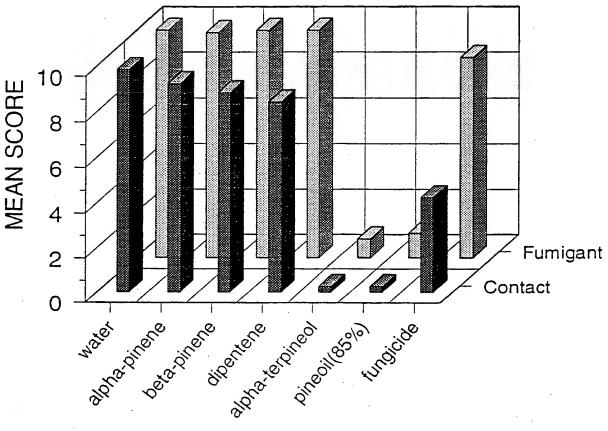
EFFECTS OF VARIOUS TREATMENTS ON FUNGAL **GROWTH**



TREATMENTS

Figure 7

EFFECTS OF VARIOUS TREATMENTS ON FUNGAL GROWTH (Mean of four Fungi)



TREATMENTS